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QUANTITATION OF POLLUTANTS IN SUSPENDED MATTER AND WATER FROM PUGET SOUND

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Report Submitted to
MESA Puget Sound Project
MARINE ECOSYSTEMS ANALYSIS PROGRAM
ENVIRONMENTAL RESEARCH LABORATORIES

by

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ABSTRACT

Puget Sound waters contained suspended matter uncontaminated by metals except for Elliott and Commencement Bays. Five metals [arsenic (As), copper (Cu), lead (Pb), antimony (Sb) and zinc (Zn)] were elevated in suspended matter collected at stations in Elliott and Commencement Bays compared to control locations in Puget Sound and the Pacific Northwest. All of these metals are on the EPA list of priority pollutants.

During July - November 1979, eighteen chlorinated compounds were detected in suspended matter collected from Hylebos Waterway which discharges into Commencement Bay. Gas chromatographic analysis suggests these compounds are also present in suspended matter sampled from Blair Waterway located adjacent to Hylebos Waterway and in the corresponding filtered waters as analyzed by a method employing XAD-2 resin adsorption. The compounds ranged from two to seven carbon atoms and consisted of alicyclic and/or cyclic chlorinated olefins and trichlorinated, tetrachlorinated and pentachlorinated benzenes. Two of these compounds have been positively identified in suspended matter (tetrachloroethylene and hexachloro-1,3-butadiene) and are on EPA's list of priority pollutants. In addition to tetrachloroethylene, 1,2-dichloroethylene, trichloroethylene, chlorodibromomethane and bromoform were also detected and quantified in waters collected from Hylebos Waterway during the same sampling periods by a "purge and trap" technique. These compounds are also on EPA's list of priority pollutants. With the exception of Blair Waterway, all of the above halogenated compounds were not detected in suspended matter or water collected at the other sampling stations monitored in this study.

In addition, five or more of a list of nine aromatic hydrocarbons (naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene) were identified in suspended matter from each sampling site and are among the list of compounds on EPA's priority list.

The saturate hydrocarbon content of suspended matter appeared to reflect biogenic distributions and concentrations with the exception of Hylebos and Blair Waterways where saturate hydrocarbon distributions indicated input of petroleum or its refined products.

These results are further discussed with respect to environmental impact and the planning of future research studies in Puget Sound by the NOAA/MESA Puget Sound Project.

SUMMARY

The specific goals of the NOAA/MESA Puget Sound Project are to: 1) assess critical environmental problems in Puget Sound waters, 2) determine the effects of critical environmental stress within the Puget Sound ecological systems and 3) identify and characterize the major marine components and processes of Puget Sound ecosystems which are involved in critical environmental problems.

The objectives of this study were intended to: 1) provide preliminary information regarding significant pollution levels in areas of Puget Sound and 2) provide a chemical base for aiding in the design of future research directed toward meeting the above goals of the NOAA/MESA Puget Sound Project.

In July 1979 water and suspended matter collected from nine sampling stations located in Elliott Bay, Commencement Bay, Sinclair Inlet, Budd Inlet and a reference area (Port Madison) were analyzed for saturate, aromatic and halogenated hydrocarbons and purgable organic compounds. Two of the sampling stations in Commencement Bay (Hylebos Waterway and Blair Waterway) appeared to be the most contaminated of the nine areas sampled, therefore, additional samples were taken at these sites in September and November 1979.

The majority of Puget Sound waters examined contained suspended matter which was not elevated in metals concentrations. Five metals (As, Cu, Pb, Sb and Zn) out of a total of 22 detected were elevated in suspended matter collected at stations in Elliott and Commencement Bays relative to stations at the other locations in Puget Sound and the Pacific Northwest. All of these metals are on the EPA priority pollutant list.

The saturate hydrocarbon content of suspended matter appeared to reflect biogenic distributions of hydrocarbons with the exception of Hylebos Waterway and Blair Waterway (Commencement Bay) where saturate hydrocarbon distributions indicated input of petroleum or its refined products.

In suspended matter, aromatic hydrocarbons from naphthalene to pyrene were present at all sampling stations whereas the higher molecular weight aromatic compounds (benz(a)anthracene, chrysene, benzo(a)pyrene and perylene) appeared to be site specific. Nine of the aromatic hydrocarbons identified are on EPA's list of priority pollutants. Negligible amounts of saturate hydrocarbons (<1-4 parts per trillion, ppt) and only trace amounts of aromatic hydrocarbons (100-300 ppt) were detected in water samples collected from Puget Sound.

Variation in the concentrations of saturate and aromatic hydrocarbons associated with suspended matter with time was complicated by large standard errors which can be rectified in the future by adoption of a more intensive sampling program.

Several classes of halogenated compounds were present in the water and suspended matter from stations in Commencement Bay (Hylebos Waterway, Blair Waterway) relative to nondetectable levels at the other stations. Eighteen

chlorinated compounds were detected in suspended matter from Hylebos Waterway. The compounds ranged from two to seven carbon atoms and consisted of chlorinated alicyclic and/or cyclic olefins and chlorinated benzenes. The concentrations of these compounds in suspended matter and water varied with time (July 1979 - November 1979) with the highest concentration levels appearing in samples collected in September and the lowest concentrations appearing in samples collected in November. These changes could not be correlated with an input of fresh water. Tetrachloroethylene and hexachloro-1,3-butadiene (on EPA's list of priority pollutants) were positively identified as two of the 18 halogenated compounds present in suspended matter. Determination of the distribution of hexachloro-1,3-butadiene between water and suspended matter indicated that a majority of the compound was present in the water. Although these compounds were present in very low concentrations, recently reported acute toxicity and bioaccumulation data with similar compounds, suggests a need for further study with respect to toxicity and possible food chain transfer.

Polychlorinated biphenyls and other halogenated pesticides commonly found in the environment were not detected in water or suspended matter from the nine sampling stations. Minimum detectability limits for these compounds in water were 0.5-1.0 ppb and 2-4 parts per billion (ppb) in suspended matter.

Only Hylebos Waterway contained quantifiable amounts of purgable organic compounds. 1,2-Dichloroethylene and trichloroethylene were present in all samples analyzed in July, September and November whereas other compounds were intermittent (tetrachloroethylene, chlorodibromomethane and bromoform). All of these compounds are on EPA's list of priority pollutants. The fact that Hylebos Waterway contained the highest concentrations of purgable halogenated compounds appears significant since it is the same location where the highest concentrations of halogenated olefins and chlorinated benzenes were found. It is also significant that the concentrations reported are significantly higher than levels reported for other water bodies which receive or have the potential of receiving industrial effluent discharges.

1. INTRODUCTION AND OBJECTIVES

Coastal zones such as Puget Sound are very attractive areas for the location of heavy industry. Increased pollution inputs from such industry, plus the waste effluents derived from municipal sewage may have significant environmental impact with time in these areas. The MESA Puget Sound Project, a small short term project (5-8 yr), was established within the Marine Ecosystems Analysis Program (MESA), a part of the National Oceanic and Atmospheric Administration (NOAA), to focus scientific research on specific environmental problems relating to Puget Sound. The specific goals of the project were to: 1) assess critical environmental problems in Puget Sound waters, 2) determine the effects of critical environmental stress within the Puget Sound ecological systems, and 3) identify and characterize the major marine components and processes of Puget Sound ecosystems which are involved in critical environmental problems.

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This report discusses the results of a study initiated to examine the distributions of volatile organic compounds in water and suspended matter and distributions of metals in suspended matter from nine sampling areas in Puget Sound. The chemical data generated in this study provides information necessary for aiding in the design of future research directed toward meeting the above goals of the NOAA/MESA Puget Sound Project.

Suspended matter is important in both the removal of pollutants from sea water, and as a food source for marine animals, making it an important mechanism by which pollutants are transported in the food web (National Academy of Sciences, 1975). Since suspended matter is the major source of material to fine-grained sediments, the chemical composition of suspended matter and fine grained bottom sediments can be expected to be highly correlated. In an estuary such as Puget Sound, a detailed characterization of the distribution of pollutants between seawater and suspended matter will contribute to the identification of both contaminants in the water and possible sources of these contaminants. Knowledge of these equilibria combined with sedimentation rates will provide needed information on the overall rates of removal of specific pollutants from seawater, their rate of accumulation in sediments and the importance of each compartment (seawater, suspended particulate matter, sediment) in the bioavailability of pollutants to marine organisms.

Many studies have been conducted which have examined the organic pollutant composition of waters (Helz and Hsu, 1978; Schwarzenbach et al., 1978; Shaw and Baker, 1978; Anderson et al., 1979) and sediments (Windsor and Hites, 1979; Hurtt and Quinn, 1979; Shaw and Baker, 1978) of large water bodies, many of which have been associated with oil spills (Burns and Teal, 1979; Keizer et al., 1978; The Amoco Cadiz oil spill, NOAA/EPA Special Report, 1978). However, there is very little data available regarding organic (Bates and Carpenter, 1979; MacLeod et al., 1976; Riley et al., 1979; Pavlou and Dexter, 1979; Brown et al., 1979) and metal pollutants (Schell and Nevissi, 1977; Crecelius et al., 1975) of Puget Sound. Even less is known about the pollution chemistry of suspended matter of large water bodies (Disalvo and Guard, 1975) including Puget Sound (Baker et al., 1978). All of the chemical data on Puget Sound indicates most areas to be relatively uncontaminated; however, a variety of pollutants have been shown to be released in the industrialized urban areas.

This study was initiated in June 1979. The following program objectives were carried out at nine sampling sites in Puget Sound in July 1979 and then again in September and November 1979 to resample at two sites in Commencement Bay.

- Determine the concentration of certain elements in suspended matter for the purpose of comparing the relative quantity and quality of metal contamination.
- Characterize and quantitate volatile saturate and aromatic hydrocarbons (including nonpurgable chlorinated hydrocarbons) in suspended matter and water.

- Characterize and quantitate volatile hydrocarbons (purgable hydrocarbons and halogenated organics) in water.
- Compare, where possible, the concentrations of hydrocarbons and halogenated organics found in suspended matter and water, and based on their distribution, determine the relative importance of these compartments as retainers of hydrocarbon pollutants.
- Determine the contribution that the hydrocarbons make to total dissolved organic carbon.
- Based on an evaluation of data generated in the July sampling, select the two most contaminated areas and resample these areas to determine the relative persistence of pollutants with time.
- Provide an adequate data base to NOAA representatives for use in future development of the technical plan for the MESA Puget Sound Project.

2. GENERAL SAMPLING STRATEGY

Sampling was conducted from an anchored research vessel. Suspended matter was collected for organic chemical analysis by pumping seawater through glass filters. Suspended matter was collected for metals analysis by pressure filtration using membrane filters. Dissolved hydrophilic organic compounds were collected by pumping glass filtered seawater through stainless steel columns packed with XAD-2 resin. Samples of water for analysis of purgable organic compounds were collected by sealing with septum caps glass bottles that were completely filled with seawater. Conventional methods were used for sampling and analysis of chlorophyll, particulate organic carbon, dissolved organic carbon, salinity, and dissolved oxygen (see Appendix A for details of sampling methods).

A brief summary of the analytical methods is presented here (see Appendix B for details of analytical methods). Elemental analysis of suspended matter was by instrumental neutron activation and energy dispersive x-ray fluorescence. Purgable organics were sparged from seawater with a stream of nitrogen gas and adsorbed on a Tenax column. Characterization and quantitation of these compounds were determined by their release from the Tenax resin into a gas chromatographic column mounted in a gas chromatograph/mass spectrometer (GC/MS). Dissolved lipophilic organic compounds that had been preconcentrated on columns containing XAD-2 resin were eluted with ethyl ether. The concentrated ether extract was separated into saturate and aromatic hydrocarbon fractions by silica gel chromatography. Saturate hydrocarbons were separated and quantitated by capillary gas chromatography (GC) using flame ionization detection (FID). Prior to capillary gas chromatography, the aromatic fraction was split into two equal fractions. One fraction was used to separate and quantitate aromatic hydrocarbons using FID; the other for the

analysis of halogenated organic compounds using an electron capture detector. Suspended matter was soxhlet extracted with benzene/methanol. The concentrated extracts were prepared for analysis of saturate, aromatic and halogenated compounds by GC as described above for the filtered water samples. GC/MS was used for the absolute identification of selected aromatic and halogenated compounds. The overall sampling and analytical scheme is shown in Fig. 1.

The sampling areas were selected to include the major industrial harbors of Puget Sound and a reference, or background, area. The four main sampling areas were: Elliott Bay (Seattle); Commencement Bay (Tacoma); Budd Inlet (Olympia); and, Sinclair Inlet (Bremerton). The reference area was Port Madison. Nine sampling stations were selected by mutual agreement between the National Oceanic and Atmospheric Administration and Battelle-Northwest. Three stations each were chosen in Elliott Bay and Commencement Bay, with one station in each of the other three areas. All sampling stations were also used by the National Marine Fisheries Service for seasonal collections of organisms and sediments for the NOAA/MESA Puget Sound Project.

The names we used for the nine stations are listed below. A general map showing the four main sampling areas and the reference area is shown in Fig. 2. Maps showing the specific locations of sampling sites are shown in Appendix C.

<u>Sampling Area</u>	<u>Station Name</u>
Elliott Bay	Pier 54 Harbor Island West Waterway
Commencement Bay	Puyallup River Hylebos Waterway Blair Waterway
Sinclair Inlet	Bremerton
Budd Inlet	Olympia
Port Madison	Port Madison

All stations were sampled July 4-7, 1979. Then, based on analysis of the chemical data from the July samples, Hylebos and Blair Waterways were selected for additional sampling. Hylebos and Blair Waterways were sampled September 25 and November 15, 1979 to determine the presence of chemicals in suspended matter and in the water with time.

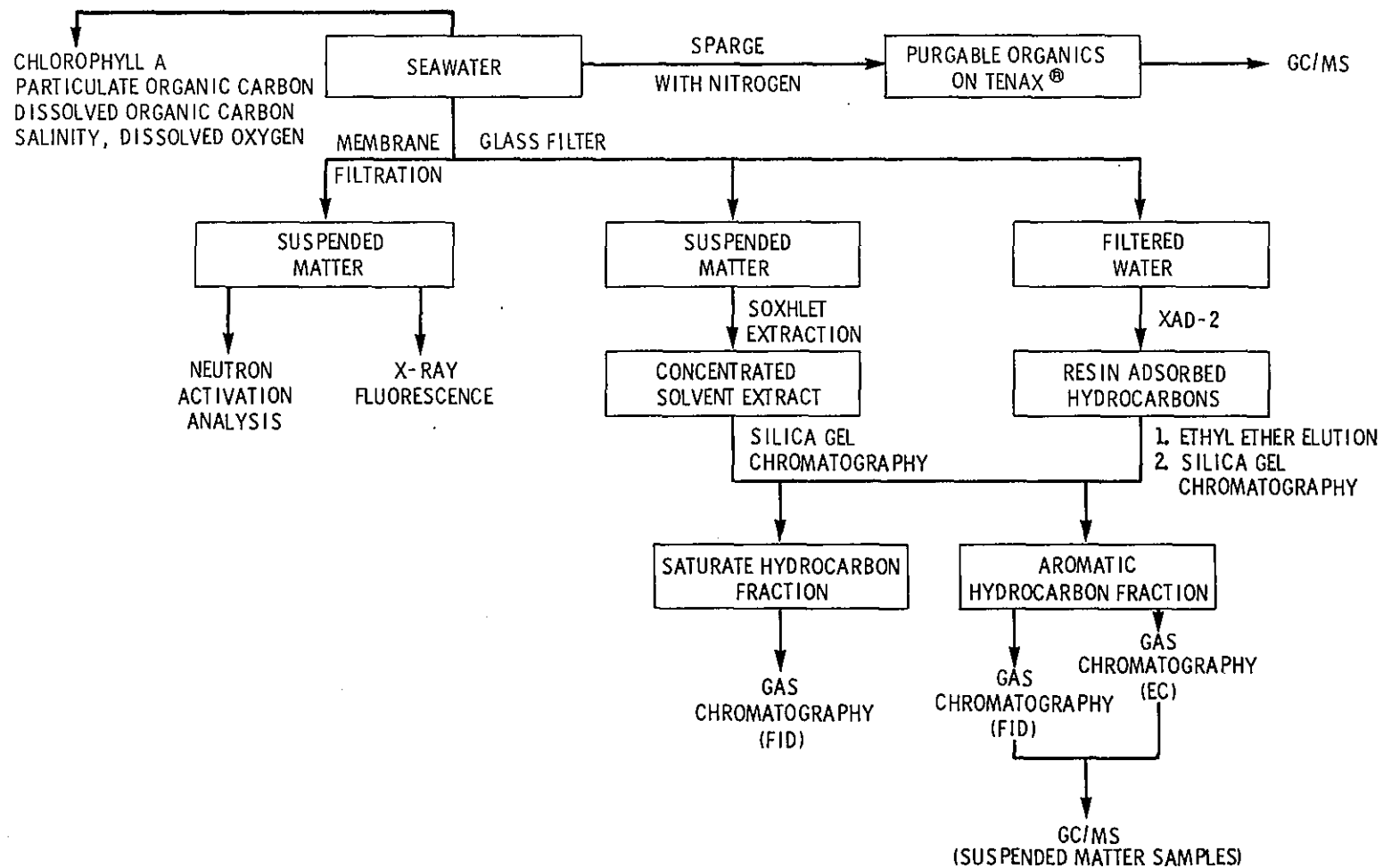


Figure 1. Sampling and analytical scheme. The aromatic hydrocarbon fraction isolated from water and suspended matter contained the aromatic hydrocarbons (benzene → benzo(a)pyrene) and the halogenated organics (alicyclic and/or cyclic halogenated olefins and chlorinated benzenes).

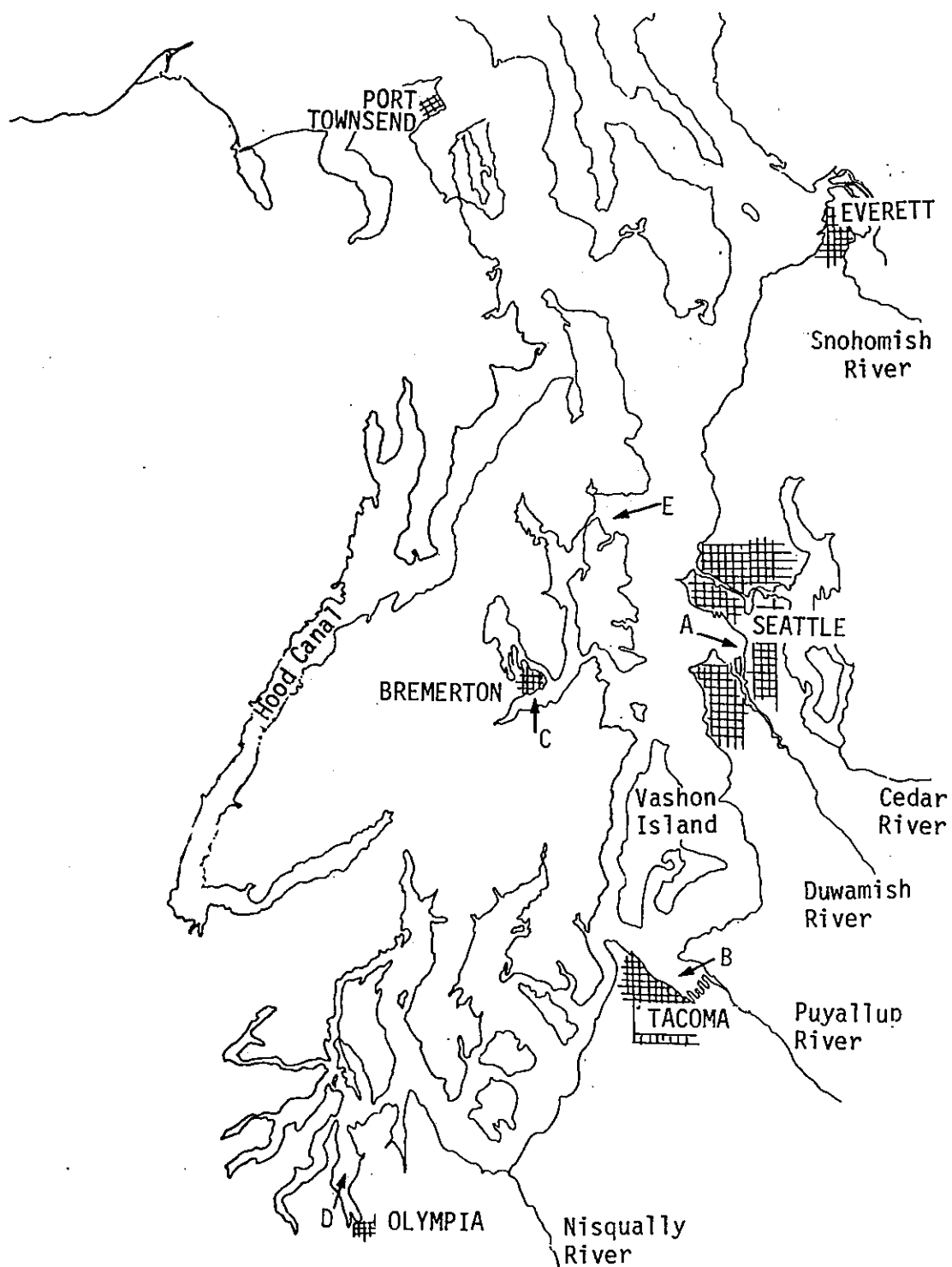


Figure 2. General map showing four main sampling areas: Elliott Bay (A), Commencement Bay (B), Sinclair Inlet (C), Budd Inlet (D) and Port Madison (E).

3. RESULTS

3.1 Spatial and Temporal Variations of Suspended Load, Chlorophyll A, and Physical and Chemical Parameters

The suspended matter load values generally ranged between 1-9 mg/l except for a value of 29 mg/l at the Puyallup River station. The percentage of organic carbon ranged from 1 to 13%.

The temperature and salinity are typical values for the time of the year. The low salinity at the Puyallup River station indicates that the sample was predominately river water. Dissolved oxygen (DO) levels were generally high or supersaturated due to oxygen production by phytoplankton. The highest DO value was at Olympia where the highest chlorophyll A values were also measured (Table 1). Dissolved organic carbon showed little variability, whereas particulate organic carbon ranged an order of magnitude and was related to suspended matter load.

3.2 Metals in Suspended Matter

3.2.1 Concentration of Metals in Suspended Matter: Variation Among Nine Sampling Sites (July 1979)

The metals that appear to be elevated due to man's activities are As, Cu, Pb, Sb and Zn (Table 2). These five metals are enriched by not more than a factor of 5 over reference levels in the industrial harbors of Seattle and Tacoma. Since the within station concentration variation is approximately +20% for one standard deviation, variability of less than 20% between stations should not be considered significant. The concentrations of all the elements determined at the nonindustrial stations (Olympia and Port Madison) were similar to those reported for suspended matter from "clean" stations such as Sequim Bay, WA and the Washington Coast (Crecelius, unpublished data). The relative proportion of Al, Fe, Si and Ti, and nearly all other elements analyzed, is fairly constant (Table 3).

3.2.2 Variability of Metals in Suspended Matter with Time

The seasonal changes in the metals content of suspended matter from Hylebos and Blair Waterways are small, if any (Table 4 and 5). Some metal concentrations were highly variable (factor of 2) but do not correlate with any known factors.

3.2.3 Intercomparison of Analytical Methods for Elements in Sediments

As part of an intercomparison of analytical methods, Battelle-Northwest (BNW) analyzed three Puget Sound sediments that had been collected and analyzed for a large number of elements by the National Marine Fisheries Service (NMFS) of Seattle. The results of the elemental analysis of sediments by BNW and NMFS are shown in Table 6. The BNW results were produced by instrumental

neutron activation analysis (INAA) for Al, Na, and Sb and by x-ray fluorescence (XRF) for the other elements (see Appendix B for details). The NMFS results were produced by plasma emission analysis of an acid leach of the sediments whereas the BNW results are for total element in sediment. In the acid leach procedure, only the portion of elements that are dissolved by an acid digestion of the sediment are quantified. The proportion of elements that dissolve varies from sediment to sediment.

Since the acid leach procedure does not allow quantification of total elemental concentrations in sediments, some discrepancy between the two laboratory's results may be expected. The elements that show fair agreement between laboratories are Cu, Fe, Ni, Pb, V, and Zn.

3.3 Halogenated Organic Compounds in Water and Suspended Matter (Qualitative)

3.3.1 Electron Capture Gas Chromatographic Studies

Electron capture gas chromatographic analysis of the aromatic fractions from XAD-2 resin concentrates of organics in water collected from nine stations in Puget Sound indicated that seven of the nine sites were relatively uncontaminated with respect to the presence of halogenated compounds. Representative examples from two of these sites (Port Madison and Pier 54) are shown in Fig. 3. Both Hylebos Waterway and Blair Waterway contained components exhibiting electron-capturing characteristics in the water. Both chromatographic patterns were similar with water from Hylebos Waterway containing higher concentrations of the components (Fig. 4). Similar patterns of electron-capturing components were observed in extracts of the suspended matter from these two stations (Fig. 5). On a qualitative basis, there were higher concentrations of these components in suspended matter from Hylebos Waterway as compared to Blair Waterway. Although the distributions of these components were different in the water column and suspended matter (because of difference in water solubility, adsorption to suspended matter and XAD-2 resin and volatility), many of the components found in the suspended matter from these two sites also appeared in the water (Fig. 6 and 7).

Electron-capture gas chromatographic analysis showed the halogenated compounds to be present in samples collected from water and suspended matter from Hylebos Waterway and Blair Waterway in July, September and November 1979. Qualitatively, the concentration levels of halogenated compounds in water and suspended matter were greatest in September with the lowest concentrations observed in waters and suspended matter examined in November (Fig. 8-11). The possibility that the drop in the levels of these compounds was a result of a pulse of fresh water was ruled out because no simultaneous drop in polycyclic aromatic hydrocarbons (PAH) were observed at these stations. In fact, PAH concentrations were at their highest levels during the November sampling. Discussion earlier in the year of some of our preliminary findings with Don Brown of NMFS, Seattle, indicated that he had found a pattern of halogenated components in bottom sediments from the same locations, several of

which he had tentatively identified as chlorinated butadienes by gas chromatography/mass spectrometry (GC/MS). We compared the retention time of electron-capturing components in water and suspended matter from Hylebos Waterway and Blair Waterway with the retention time of synthetic hexachloro-1,3-butadiene. A component which matched the retention time of hexachloro-1,3-butadiene was found in the water and suspended matter of Hylebos Waterway and Blair Waterway although the component in the water of Blair Waterway was small (Fig. 12-15).

3.3.2 Characterization and Quantitation of Halogenated Organics in Suspended Matter and Water of Puget Sound

Polychlorinated biphenyls (PCB's) and other halogenated pesticides were not detected in water or suspended matter sampled from the nine stations in July 1979 and again at two of these stations (Hylebos Waterway and Blair Waterway) sampled in September and November 1979. Although several of the peaks in electron-capture gas chromatograms of extracts of suspended matter from Hylebos Waterway matched the relative retention times of known halogenated pesticide standards, none had spectra which matched the published mass spectra of the common halogenated pesticides (Knight and Bonelli, 1971). Minimum detectability limits for these halogenated pesticides in the water were 0.5-1.0 ppb and 2-4 ppb in suspended matter. Since samples of suspended matter from Hylebos Waterway contained the highest concentrations of halogenated compounds we elected to emphasize the analysis of this material for tentative and absolute characterization of halogenated compounds by GC/MS. Fig. 16 shows the electron-impact total ion chromatogram of the aromatic fraction of suspended matter from Hylebos Waterway and a list of compounds tentatively identified. Analysis of spectra indicated the only detectable halogen present in the compounds associated with this suspended matter was chlorine. Compounds designated by a letter contained chlorine and were assigned molecular formulas and possible structural formulas based on comparison of chlorine isotope ratios of the unknown compounds to known literature values (McLafferty, 1967). Mass spectra of chlorinated compounds tentatively identified are found in Appendix C. The chlorinated compounds listed in Fig. 16 can fall into several possible structural types. These include chlorinated alicyclic mono, di and polyolefins and/or chlorinated cyclic olefins and chlorinated benzenes. Hexachloro-1,3-butadiene and tetrachloroethylene were the only chlorinated compounds positively identified and quantitated in suspended matter from Hylebos Waterway based on congruency of relative retention times by gas chromatography and congruency of mass spectra of unknown and analytical standard. Fig. 17 shows the spectra match for hexachloro-1,3-butadiene. Since the response of the electron capture detector varies considerably with the number of chlorine atoms in the compound, it is important that analytical standards be available to confirm absolute structures and to be able to determine accurately their concentrations in suspended matter and water. Therefore, absolute confirmation of structures of chlorinated compounds and their concentrations in water and suspended matter in Hylebos and Blair Waterways has to await the availability of analytical standards. Since GC/MS characterization of halogenated compounds in suspended matter from Blair Waterway was not conducted and waters from these two waterways contained concentrations of halogenated

compounds too low for GC/MS analysis, we can only suggest that these as well as other chlorinated hydrocarbons yet to be identified are responsible for the electron-capture activity observed in these waters and suspended matter. Such assumptions are not unreasonable, bearing in mind that electron-capturing compounds in GC chromatograms of extracts from Hylebos Waterway match the relative retention times of electron-capturing compounds found in the suspended matter from Blair Waterway and their corresponding filtered waters. Table 7 lists the concentrations and distributions of hexachloro-1,3-butadiene found in suspended matter and water from Hylebos Waterway and Blair Waterway based on the above assumptions. Concentrations in the water ranged from <0.1 to 0.6 ppb for Blair Waterway and 0.2 to 2.4 ppb in Hylebos Waterway. Concentrations of hexachloro-1,3-butadiene in suspended matter from Blair Waterway ranged from 1.0 to 3.0 ppb to 9.9 to 148 ppb in Hylebos Waterway. Based on its distribution, most of the hexachloro-1,3-butadiene appeared to be in the water. These distributions, however, have to be viewed with caution because they are dependent on variations in the total concentration of hexachloro-1,3-butadiene and suspended load present with time.

3.4 Concentrations of Purgable Organic Compounds in Water from Puget Sound (Characterization and Quantitation)

The results of our analysis of Puget Sound waters for organic compounds using a "purge and trap" technique are shown in Table 8. Examination of data obtained from the July sampling trip showed that only Hylebos Waterway contained quantifiable amounts of purgable organic compounds. 1,2-Dichloroethylene, trichloroethylene and bromoform were present in a concentration range of 0.8 to 1.1 ppb. Tetrachloroethylene and chlorodibromomethane were detectable in single ion mass spectrometric scans, but were not present in sufficient concentration to quantitate. Combinations of these same compounds were detectable, but not quantifiable at the other eight sampling sites. Similar results were obtained when Blair Waterway and Hylebos Waterway were sampled again in September and November to determine the variation in the concentrations of these compounds with time. Again, only Hylebos Waterway contained sufficient concentrations of compounds to quantify. 1,2-Dichloroethylene and trichloroethylene were present in quantifiable amounts in water samples collected from Hylebos Waterway from all three time periods. Concentration ranges were 0.8-2.4 ppb and 0.8-3.0 ppb for 1,2-dichloroethylene and trichloroethylene respectively. Quantifiable amounts of tetrachloroethylene were present in waters from the September 1979 (0.4 and 0.3 ppb) sampling trip but not in July and November and in only one instance was chlorodibromomethane quantifiable (Sept. 1979). The concentrations of bromoform in waters from Hylebos Waterway were in the range of 0.7-1.2 ppb during July 1979 and September 1979 but dropped below quantifiable levels in November 1979. Carbon disulfide was present; however, it was not quantitated because it is believed to be an artifact of the sampling apparatus. Lastly, methylene chloride was not quantifiable in two instances due to overlap of the methylene peak with artifacts derived from septum bleed. Therefore, the concentrations, in many cases, reported for methylene chloride are disproportionately high and must be viewed with caution. (Septum bleed results in the release of volatile organic

artifacts into the gas chromatographic column. The extent of this release depends on septum conditioning, which can be quite variable). We also examined waters from Blair Waterway and Hylebos Waterway for volatile low molecular weight chlorinated butadienes using the "purge and trap" technique and using 2-chloro-1,3-butadiene and 2,3-dichloro-1,3-butadiene as standard compounds. These compounds were not found in the GC/MS chromatograms obtained from these samples.

3.5 Saturate and Aromatic Hydrocarbons in Puget Sound Water (Characterization and Quantitation)

Table 9 shows the concentrations of saturate hydrocarbons isolated from samples of water collected from nine stations in Puget Sound (July 1979). In all cases, the saturate hydrocarbon concentrations ($C_{13} \rightarrow C_{24}$, pristane, phytane) were below minimum detectable limits of $<2-4$ pptr. Similar results were observed for saturate hydrocarbons isolated from waters from Blair Waterway and Hylebos Waterway when monitored with time. Concentrations were below the minimum detectability limits of $0.2-3$ pptr (Table 10).

Concentrations of selected aromatic hydrocarbons isolated from samples of filtered water from the same nine sampling stations are listed in Table 11. Concentrations of compounds from naphthalene to pyrene were in the range of $1-108$ pptr. Because of the large standard error associated with individual data points, no significance can be attached to variation in mean concentrations observed between stations. Higher molecular weight aromatic hydrocarbons (fluoranthene, 1-methylpyrene, benz(a)anthracene and chrysene) were not present at detectable levels (<1 pptr). Comparison of the concentrations of aromatic hydrocarbons in samples of water collected from Hylebos Waterway and Blair Waterway showed the waters sampled in July to contain the highest concentrations of aromatic hydrocarbons which were in the range of $2-74$ pptr. No aromatic hydrocarbons were detected in water samples from the July 1979 sampling ($<2-4$ pptr) and only trace amounts of naphthalene and the methylnaphthalenes were detected in samples from the November collection. As in the July sampling, the higher molecular weight aromatic hydrocarbons were not detected (Table 12).

3.6 Saturate and Aromatic Hydrocarbons in Suspended Matter from Puget Sound

Table 13 lists the concentrations of volatile saturate hydrocarbons isolated from suspended matter from nine stations in Puget Sound sampled in July 1979. Total saturate hydrocarbon concentrations ($C_{13} \rightarrow C_{24}$, pristane, phytane) ranged from 11.3 to 67.6 parts per million (ppm) for the nine sampling stations. The three Seattle stations appeared to have lower total concentrations of saturate hydrocarbons than either Bremerton, Olympia or the three Tacoma stations. Although the total saturate hydrocarbon concentration at the Port Madison station was high, it was due mainly to one component, pristane, otherwise the individual hydrocarbon concentrations fit more closely the

hydrocarbon concentrations determined at the Seattle stations. High standard errors were associated with the Bremerton, Olympia and Tacoma stations suggesting a high degree of variability in suspended matter type and/or concentrations of saturate hydrocarbons associated with individual suspended matter particles. Due, again, to high standard errors, no differences could be observed in hydrocarbon concentrations of suspended matter from Hylebos Waterway and Blair Waterway with time (Table 14). Fig. 18 shows typical gas chromatographic distributions of saturate hydrocarbons isolated from suspended matter in Puget Sound.

Table 15 lists the concentrations of a selected set of aromatic hydrocarbons isolated from suspended matter from nine sampling stations in Puget Sound in July 1979. Significant differences in the total concentrations of aromatic hydrocarbons were observed between sampling stations. The Tacoma sampling stations (Puyallup River, Hylebos Waterway, Blair Waterway) contained the greatest concentrations of aromatic hydrocarbons adsorbed to suspended matter (7.71, 4.08 and 7.67 ppm respectively) whereas Seattle's Harbor Island and Olympia's Budd Inlet had the least (0.90 and 1.01 ppm respectively). Aromatic hydrocarbons from naphthalene to pyrene were found at all sampling sites whereas the higher molecular weight aromatic compounds (benz(a)anthracene, chrysene, benzo(a)pyrene and perylene) appeared to be site specific. All four compounds were associated with suspended matter from Seattle's Pier 54 and Tacoma's Hylebos Waterway (0.01 - 0.13 ppm) whereas concentrations of these compounds in suspended matter from Bremerton's Sinclair Inlet, Tacoma's Blair Waterway, Olympia's Budd Inlet and Port Madison were not detected (<0.01 - 0.02 ppm). Suspended matter from Seattle's Harbor Island and West Waterway contained detectable levels of benz(a)anthracene and chrysene (0.03 - 0.12 ppm) but benzo(a)pyrene and perylene were below the limits of detectability (<0.01 ppm). Conversely, suspended matter from Tacoma's Puyallup River contained detectable levels of benzo(a)pyrene and perylene (0.12 - 0.18 ppm), but benz(a)anthracene and chrysene were below the limits of detectability (<0.01 ppm). Determination of the variations in concentrations of aromatic hydrocarbons from suspended matter from Hylebos Waterway and Blair Waterway with time was complicated by large standard errors (Table 16). Total aromatic hydrocarbons appeared to be highest in both waterways in November with these increases appearing to result from increased concentrations of the higher molecular weight aromatic hydrocarbons (benz(a)anthracene, chrysene, benzo(a)pyrene, perylene). Fig. 19 shows typical gas chromatographic distributions of aromatic hydrocarbons isolated from suspended matter in Puget Sound.

Total saturate hydrocarbons accounted for approximately 0.04 to 0.2% of the total organic in the suspended matter whereas the total aromatic hydrocarbons accounted for 0.002% to 0.01% of the total carbon.

4. DISCUSSION

The purpose of this study was to produce a preliminary data base on the concentrations of organic and inorganic pollutants associated with suspended

matter and/or water from nine sampling stations in Puget Sound. The nine sampling stations were selected by mutual agreement between the National Oceanic and Atmospheric Administration and Battelle-Northwest. Because of this, chemical data generated on suspended matter and water by our study would be compatible and complementary to data being generated by NMFS resulting from seasonal collections of organisms and sediments from the same sampling stations. The NMFS study is sponsored by MESA and is a part of the project under which Battelle-Northwest data were collected and here reported.

Concentrations of suspended matter were positively correlated with chlorophyll A and particulate organic carbon, indicating phytoplankton was a significant component. Excluding the Puyallup River station the correlation coefficient (r) for suspended load with chlorophyll was 0.76 and suspended load with POC was 0.87. The concentration of crustal elements such as Fe and Al indicated crustal material was a major contributor to the suspended matter except at Olympia and Port Madison.

The temperature and salinity are typical values for the time of the year. The low salinity at the Puyallup River station indicates that the sample was predominately river water. Dissolved oxygen (DO) levels were generally high or supersaturated due to oxygen production by phytoplankton. The highest DO value was at Olympia where the highest chlorophyll A values were also measured. Dissolved organic carbon showed little variability, whereas particulate organic carbon ranged an order of magnitude and was related to suspended matter load.

The differences that occurred between summer and fall at Hylebos and Blair Waterways are a decrease in suspended matter load with a paralleled decrease in chlorophyll A and POC due to the annual cycle of phytoplankton.

The elemental composition of Puget Sound suspended matter is controlled by pollution, river borne crustal material and biological activity. Puget Sound waters contained suspended matter uncontaminated by metals except for Elliott and Commencement Bays. Five metals (As, Cu, Pb, Sb and Zn) were elevated in suspended matter collected at stations in Elliott and Commencement Bays compared to stations at control locations in Puget Sound and the Pacific Northwest. All of these metals are on the EPA list of priority pollutants. These results support a tentative conclusion that the suspended matter in only the industrial harbors of Puget Sound are contaminated by some metals. The biological significance of these metal levels in suspended matter cannot be determined at present due to a lack of information on the cycling and bioavailability of contaminants in suspended matter to organisms. However, we would expect increased levels of some metals in animals feeding on this matter. Experiments in our laboratory have shown that a detritus feeding clam accumulated copper from copper contaminated detritus (Apts et al., 1978).

The concentrations of Al, Fe, Si and Ti in suspended matter reflect the input of crustal materials by river runoff. The relative proportion of these four crustal elements, and nearly all the other elements analyzed, is fairly constant. The absolute concentration of Fe, Al and Si decrease at stations distant from rivers (Olympia and Port Madison) due to removal of crustal

material by sedimentation and dilution by organic matter. The biogenic contribution, as determined by organic carbon and chlorophyll A, dilutes the crustal elements by a factor of 4 at Port Madison and 10 at Olympia. Some metal concentrations were highly variable; therefore, to determine any significant differences in metal concentrations with time will require a more intensive sampling program.

There appears to be a correlation between the metal levels in the suspended matter and concentrations of metals in fine grained sediments from the same area that were collected and analyzed by NMFS. The highest concentrations of heavy metals in sediments were from stations in Elliott and Commencement Bays (NMFS, Seattle, WA, unpublished results). This correlation indicates that a portion of the metal contaminants entering Puget Sound from industrial areas are removed by suspended matter and accumulated in the sediments. The biological significance of these metal levels in suspended matter cannot be determined at present because the ecological consequences of elevated metal body burden on suspension feeding animals has not been determined. However, both field and laboratory studies for selected elements would predict elevated metal levels in animals feeding on contaminated suspended matter.

Eighteen chlorinated compounds were detected in suspended matter collected from Hylebos Waterway. Two of these compounds were positively identified as hexachloro-1,3-butadiene and tetrachloroethylene. Based on gas chromatographic retention time studies, these compounds were also suggested to be present in the suspended matter of Blair Waterway as well as the corresponding filtered waters. The compounds ranged from two to seven carbon atoms and consisted of alicyclic and/or cyclic chlorinated olefins, possible discharges resulting from the Diels-Alder preparation of chlorinated pesticides (Brooks, 1974), and trichlorinated, tetrachlorinated, and pentachlorinated benzenes, which are common industrial chemicals (Sheldon and Hites, 1979). Analyses conducted by NMFS (unpublished results) has detected and quantitated dichlorobenzene, trichlorobutadiene, tetrachlorobutadiene, pentachlorobutadiene and hexachlorobutadiene in sediment from Hylebos Waterway. In addition, with the exception of dichlorobenzene, all of the chlorinated butadienes were quantifiable in sediment collected from Blair Waterway. Also analyses conducted by NMFS (unpublished results) have detected these same compounds in a variety of benthic organisms residing in sediments of Hylebos Waterway; however, the levels are lower than the levels of polychlorinated biphenyls observed on the same species. In addition, examination of demersal organisms (English and Rock Sole) collected from Hylebos Waterway showed considerable accumulation of chlorinated butadienes in their livers, especially hexachloro-1,3-butadiene (NMFS, unpublished results).

We found concentrations of hexachloro-1,3-butadiene in suspended matter from Hylebos Waterway to be similar to concentrations reported in sediment collected from Hylebos Waterway and analyzed by NMFS. The fact that this compound as well as other chlorinated olefins appear also to be present in the water suggests a pathway for transport of the pollutants from discharge effluent to suspended matter to sediment and to benthic, demersal and pelagic

organisms. EPA water quality criteria has been established for hexachloro-1,3-butadiene (EPA, Federal Register, Vol. 44, No. 52, March 15, 1979). However, extrapolations of these data to waters from Hylebos Waterway have to be viewed with extreme caution when it is known that other similar halogenated compounds are present for which acute and chronic toxicity data may not be available.

In addition to hexachloro-1,3-butadiene, and tetrachloroethylene, 1,2-dichloroethylene, trichloroethylene, chlorodibromomethane and bromoform, common to industrial discharge effluents (Perry et al., 1978) were also detected and quantified in waters collected from Hylebos Waterway. All of these compounds are on the EPA list of priority pollutants.

The fact that Hylebos Waterway was the only station that contained quantifiable levels of purgable halogenated compounds appears significant since it is the same location where the highest concentrations of halogenated olefins and chlorinated benzenes were found. It is also significant that the concentrations reported are significantly higher than levels of halogenated purgable organic compounds reported for other water bodies which receive or have the potential of receiving industrial effluent discharges (Sheldon and Hites, 1978; Bean et al., 1980).

Data produced by our study and the study conducted by NMFS and combined with information on similar chlorinated organic compounds for which bioaccumulation and toxicity data are available (Spehar et al., 1979) indicates a need for further study of these compounds with respect to fate, toxicity and potential food chain transfer. Recommendations to NOAA regarding additional studies are discussed in Section V.

Saturate and aromatic hydrocarbons in samples of water collected from nine stations in Puget Sound do not appear to pose any immediate environmental problem since they were found to be present at levels ~1000 fold less than levels used in a laboratory exposure system to study chronic and acute effects of oil exposure to pelagic marine organisms (Bean et al., 1978; Anderson et al., 1980).

The saturate hydrocarbon content of suspended matter appeared to reflect the concentrations and biogenic distributions of hydrocarbons similar to what has previously been reported (Carpenter and Fairhall, 1979) with the exception of Hylebos Waterway and Blair Waterway where saturate hydrocarbon distributions indicated input of petroleum or its refined products (Riley et al., 1979; Riley et al., 1980).

Aromatic hydrocarbons from naphthalene to pyrene were detected in samples of suspended matter collected from all nine stations whereas the higher molecular weight aromatic compounds (benz(a)anthracene, chrysene, benzo(a)pyrene and perylene) appeared to be site specific. Concentrations of aromatic hydrocarbons in suspended matter appeared to be an order of magnitude lower than concentrations observed in sediment from similar locations (Riley et al., 1980, NMFS, unpublished results). Their presence in suspended matter and their

absence at detectable levels in water suggests an efficient pathway for their transport to sediments. Recent studies in Puget Sound (NMFS, unpublished results) find these compounds most available to benthic organisms; however, limited information is available regarding sublethal effects on aquatic organisms or their transformations into major metabolites which may be more toxic than the parent compound (Neff, 1979). In addition, nine of the compounds found in suspended matter (naphthalene, anthracene, benz(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene) are on EPA's list of priority pollutants. Therefore, there is a need for additional studies on the fate and effects despite the fact that determining the origins of these compounds in large water bodies is difficult if not impossible to pinpoint (Lake et al., 1979). Recommendations to NOAA regarding additional studies in this area are discussed in Section V.

5. RECOMMENDATIONS

5.1 Halogenated Compounds in Suspended Matter and Water from Commencement Bay (Blair Waterway and Hylebos Waterway)

Preliminary studies conducted in the Commencement Bay area of Puget Sound showed the presence of chlorinated olefins in the water and suspended matter of Blair Waterway and Hylebos Waterway while other stations appear relatively uncontaminated. The concentrations of these compounds in suspended matter and water varied with time (July - September 1979) with the highest concentration levels appearing in the September sampling and the lowest concentrations appearing in November. Eighteen chlorinated compounds were detected by gas chromatograph-mass spectrometry.

A logical extension of this work, although not proposed under this study would be to proceed with the following detailed investigations. Such investigations would be of immense value in assessing the overall environmental impact of the presence of these compounds in the Commencement Bay area.

1. Continue to sample suspended matter and water from Commencement Bay this year to determine whether the chlorinated olefins continue to persist in this area. Also sample sediments.
2. Design and implement the sampling program so that the source(s) of these chlorinated olefins can better be defined.
3. Acquire additional analytical standards so that absolute characterization and quantitation of as many of the chlorinated compounds can be made. This is important in order to be able to better define the range of concentrations of chlorinated olefins present in these waterways. At present, we can only assume the concentrations to be similar to hexachlorobutadiene, the only compound in this molecular weight range that we have absolutely identified and quantitated in Commencement Bay. This assumption may or may not be valid. The

results from this study can also be used to establish guidelines for the design of acute and chronic toxicity experiments to assess biological impacts and aid in the establishment of guidelines for regulation of the amounts of these waste effluents entering Puget Sound.

4. Conduct experiments in the laboratory on the microbial degradation potential of these chlorinated olefins using suspended matter and/or sediments from Hylebos Waterway and Blair Waterway as compared to a control sediment from an area such as Port Madison. Initial experiments can be conducted with hexachlorobutadiene. Conduct these experiments in parallel with suspended matter and/or sediments using a polynuclear aromatic hydrocarbon (PAH) and a polychlorinated biphenyl (PCB). Such studies will A) produce information on the importance of the biodegradation process in controlling the persistence of these compounds in sediments, suspended matter and water of Commencement Bay, B) provide information on their susceptibility to degradation as compared to other pollutants in Puget Sound such as PAH and PCB, C) provide information on products of chlorinated olefin metabolism which may have environmental impact, and D) provide information that can be used to compare the ability of microorganism populations from Commencement Bay and control area (Port Madison) sediments to control the persistence of these compounds.
5. Validate laboratory microbial studies by screening Commencement Bay sediments for the presence of products of metabolism of chlorinated olefins identified in the laboratory experiments.
6. Conduct mutagenic assays (Ames assays) to establish the mutagenicity of identified chlorinated olefins isolated from suspended matter and/or sediment fractions relative to known mutagens (benzo(a)pyrene, 2-aminoanthracene) to assess the potential non-occupational human health effects of these compounds.

5.2 Polynuclear Aromatic Hydrocarbons (PAH) in Suspended Matter from Puget Sound

Results from this investigation have indicated that polynuclear aromatic hydrocarbons (PAH) are components present in suspended matter from Puget Sound. Recent published research was unable to assign specific origins to PAH based on their concentrations in estuarine sediments (Lake et al., 1979); therefore, it becomes questionable as to the usefulness of attempting to determine their point sources, especially from a regulatory point of view.

A more important study should focus on those processes which control the retention and fate of PAH and their associated decomposition products in the marine environment. One such study would look at the role that photooxidation and microbiological degradation processes play in the formation of oxygenated compounds and their distribution and fate in marine ecosystem compartments (water, suspended matter, and sediment).

Little research has been conducted to determine the impact of oxygenated compounds in marine ecosystems, despite the fact that these compounds have been shown to account for major fractions (50-90%) of the total organics present in particulate matter (Fox and Olive, 1979). Such fractions have been shown to possess significant carcinogenicity in biological testing. Recent Battelle-Northwest studies have reported the formation of oxygenated compounds from water-soluble phenanthrene exposed to cultures of organisms residing in Sequim Bay sediments. Furthermore, the reported sensitivity of nonpolar organics in particulate matter to ultraviolet light suggests that photooxidation may provide a significant decomposition pathway for such compounds. Most recently, several photo decomposition products of anthracene have been identified when anthracene adsorbed to air particulates was exposed to UV light. Only about 10% of the original anthracene remained. These results suggest that photooxidation can contribute significantly to the formation of oxygenated PAH sorbed to atmospheric particulates ultimately bound for transport to water bodies such as Puget Sound. Furthermore, this suggests that the common indices of potential hazard (i.e., the determination of PAH or benzo(a)pyrene concentrations in collected particulate) may be seriously underestimated. The distribution of these oxygenated constituents once the particulates impact a water body is also unknown.

A logical extension of this research would be to conduct a series of laboratory experiments coupled with eventual field validation studies, to determine the distribution and fate of PAH and their associated photodecomposition and microbiologically degraded products between water, suspended matter, sediment. Because of the need for initial control of parameters and the assurance of the formation of detectable amounts of decomposition products and the greater expense of field studies, the first phase of this study would be conducted in the laboratory followed by field validation. Air particulate samples amended with radiolabeled PAH would serve as substrates for these studies. The types of experiments to be conducted (not necessarily complete) are listed below:

1. Expose air particulates amended with radiolabeled PAH to sunlight. Characterize and determine the relative abundance of photodecomposition products formed as a function of time, intensity of light, and wavelength or irradiation.
2. Add sunlight-exposed particulates to filtered and nonfiltered Puget Sound water. Determine the distribution of PAH and associated photodecomposition products between sunlight-exposed air particulates and water and their redistribution among other suspended matter in the water as a function of temperature, EH, and particulate matter/sediment composition.
3. Incubate air particulates amended with radiolabeled PAH in water with microorganisms cultures derived from Puget Sound sediments. Determine the type and rate of formation of biodegradation products. Compare the pathway of decomposition with that of photodecomposition. Determine rates of biodegradation as a function of temperature, EH, and particulate matter/sediment composition.

4. Expose particulate matter to flowing sea water for lengths of time approximating natural suspended matter residence time in Puget Sound. Compare distribution of PAH and degradation products before and after treatment to obtain information on these components in sediment as a function of temperature, EH, and particulate matter/sediment composition.
5. Validate results produced in Experiments 1-4 by field sampling parent substrate and degradation products at a well-characterized field site.
6. Screen parent substrates and degradation products for mutagenic activity. Use these results to select those components to be tested in bioavailability studies.

These extensions of the current NOAA/MESA program should provide a sound beginning for establishing environmental impact of trace pollutants over a broad range of conditions in Puget Sound.

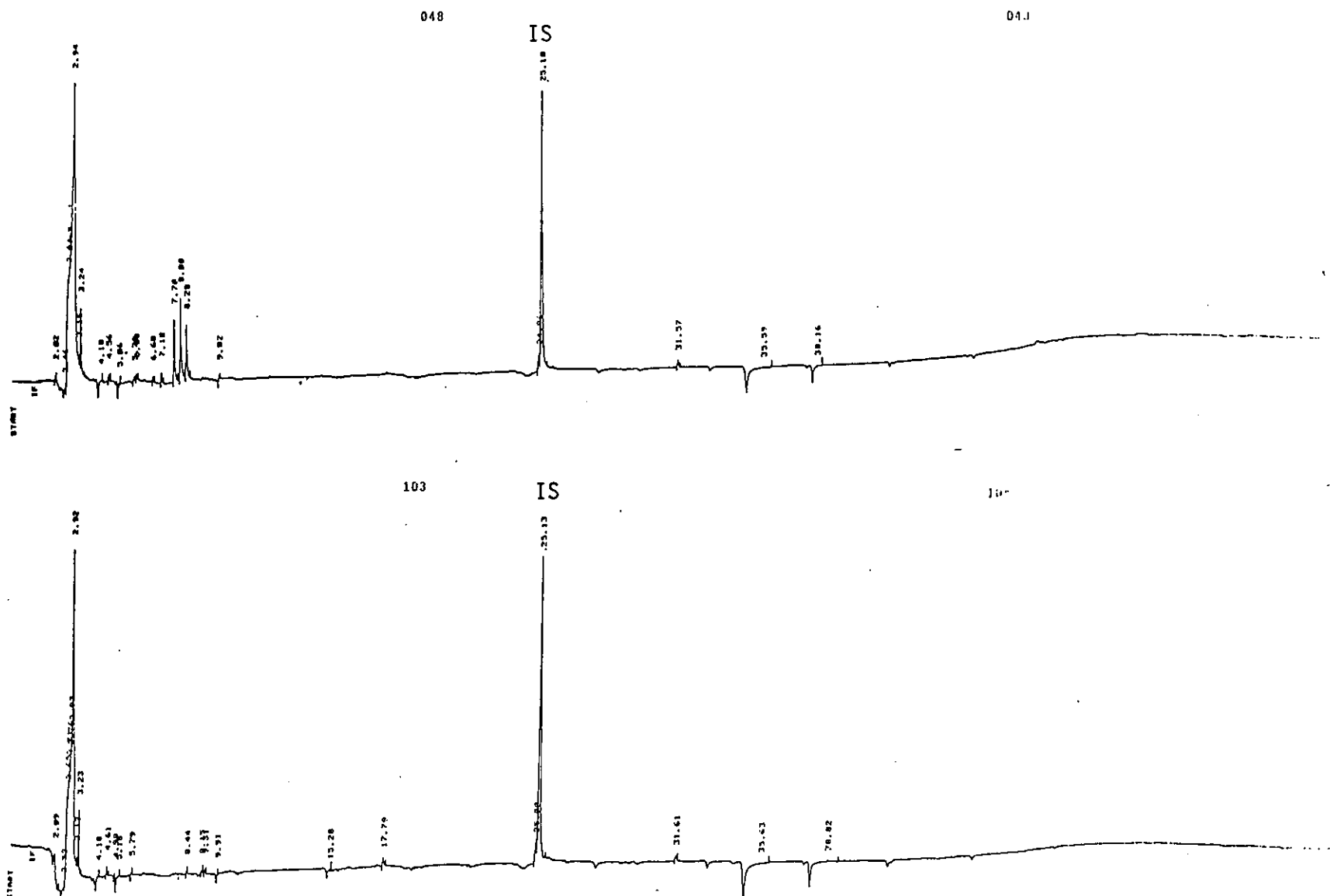


Figure 3. Electron capture gas chromatograms of extracts of water from Port Madison (top) and Pier 54 (bottom). IS = Internal Standard

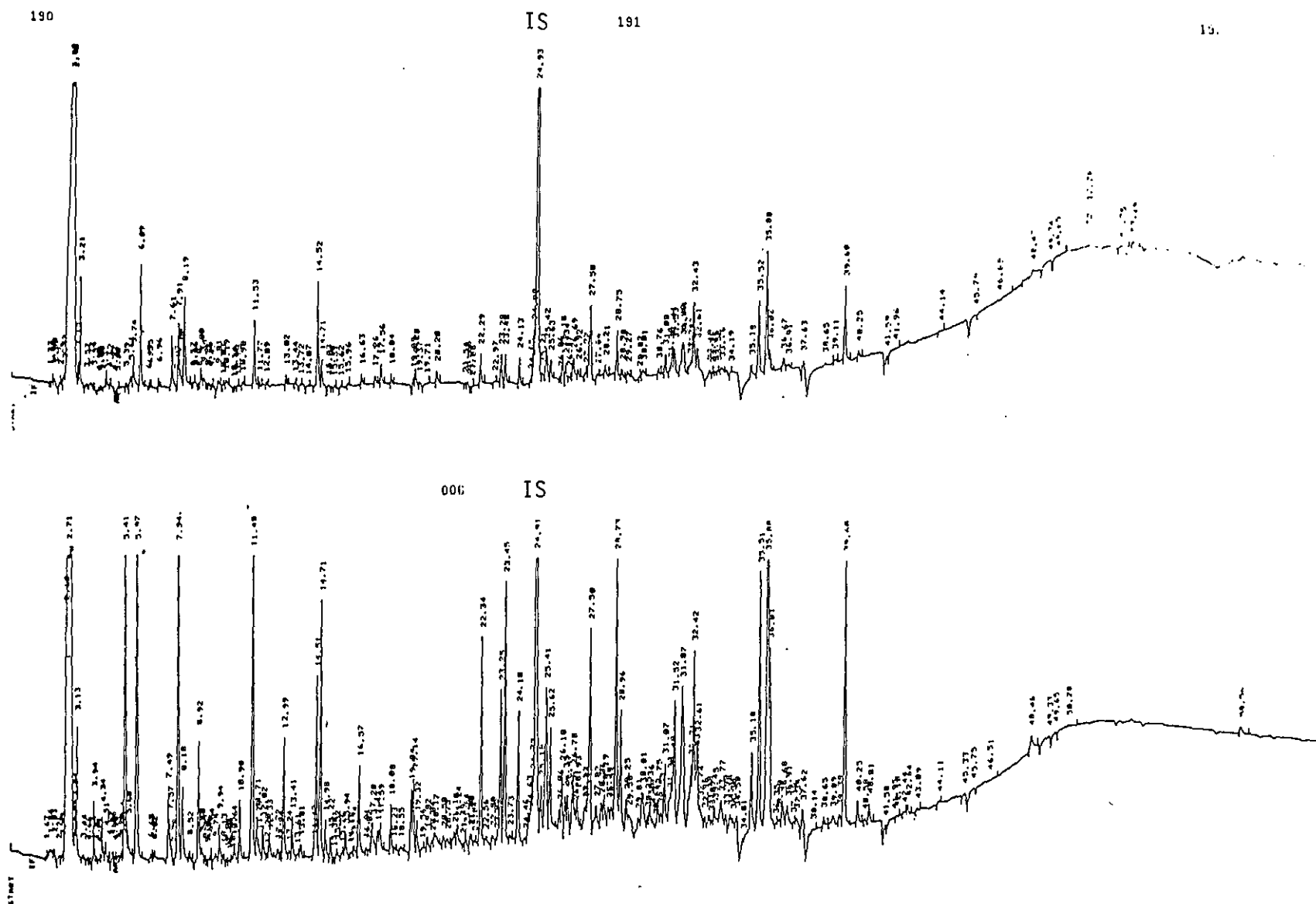


Figure 4. Electron capture gas chromatograms of extracts of water from Blair Waterway (top) and Hylebos Waterway (bottom). IS = Internal Standard

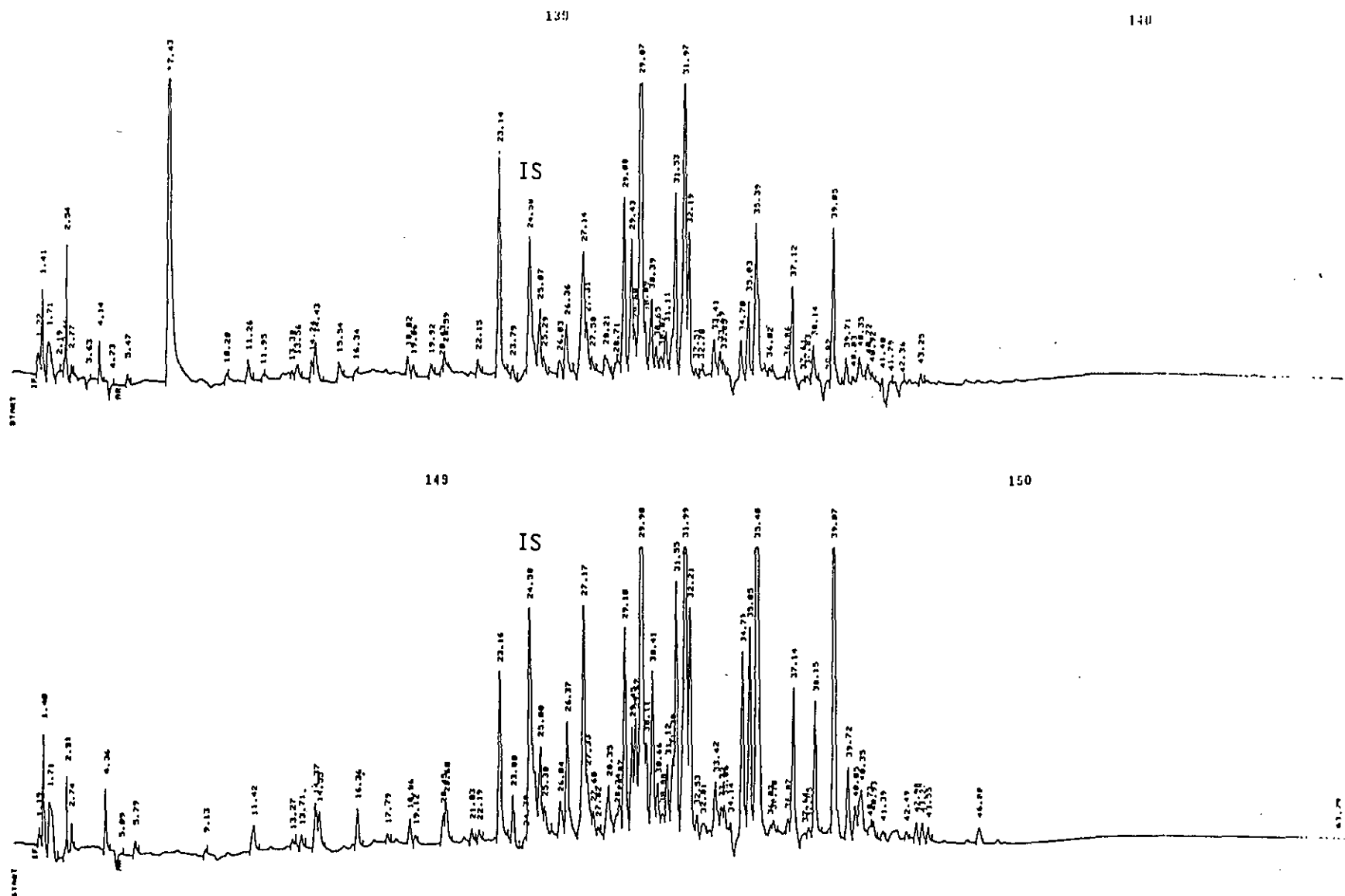


Figure 5. Electron capture gas chromatograms of extracts of suspended matter from Blair Waterway (top) and Hylebos Waterway (bottom). IS = Internal Standard

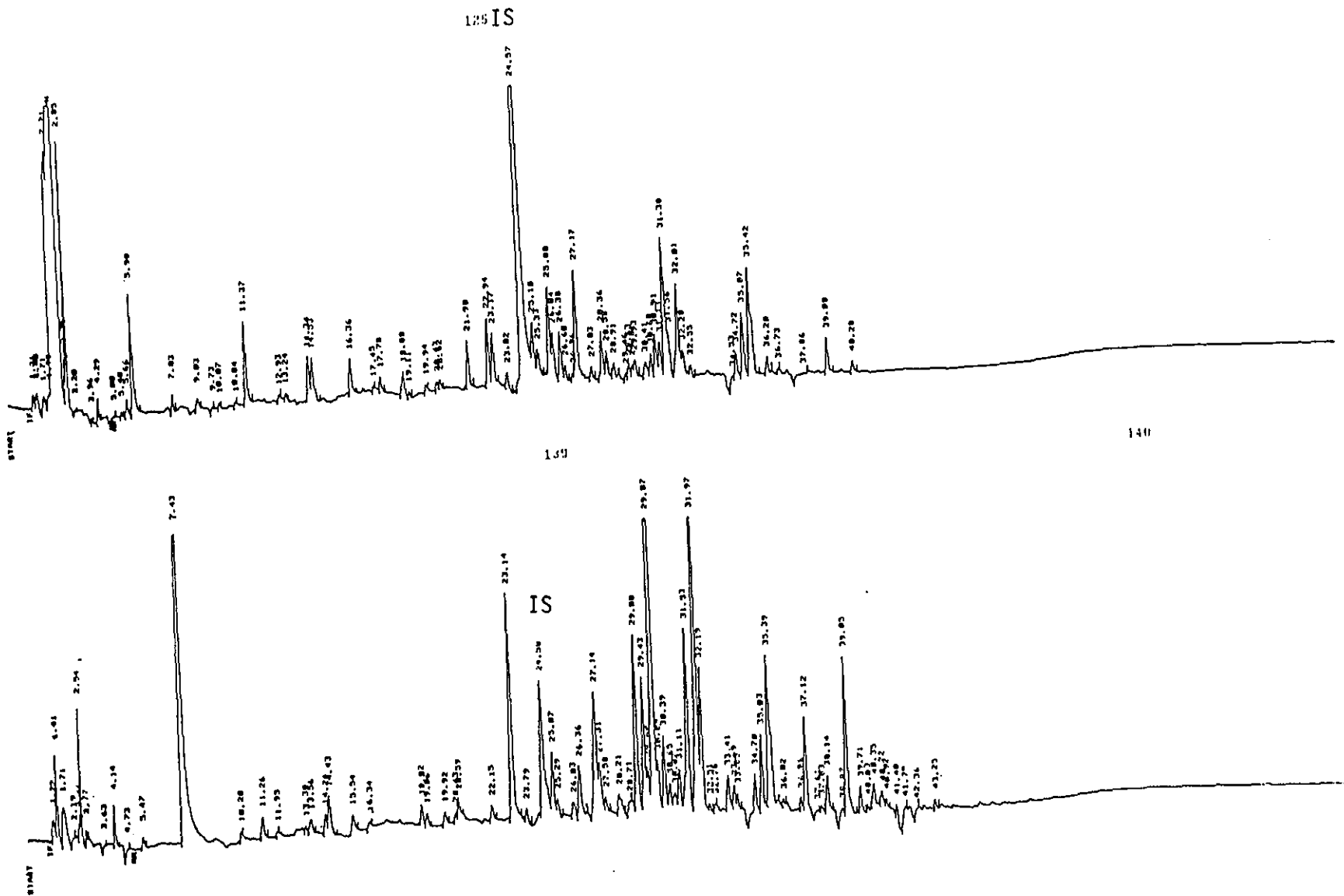
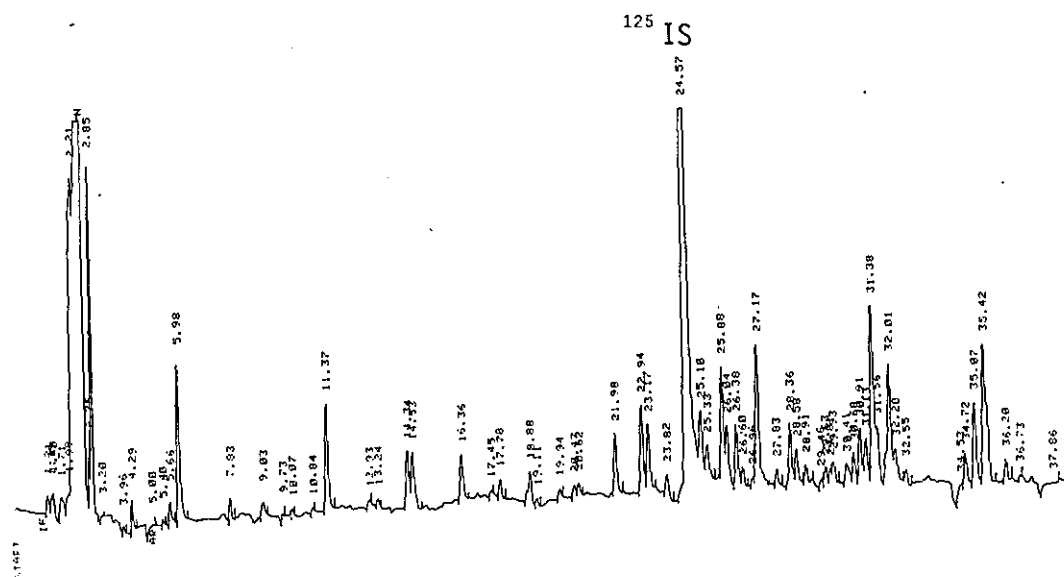
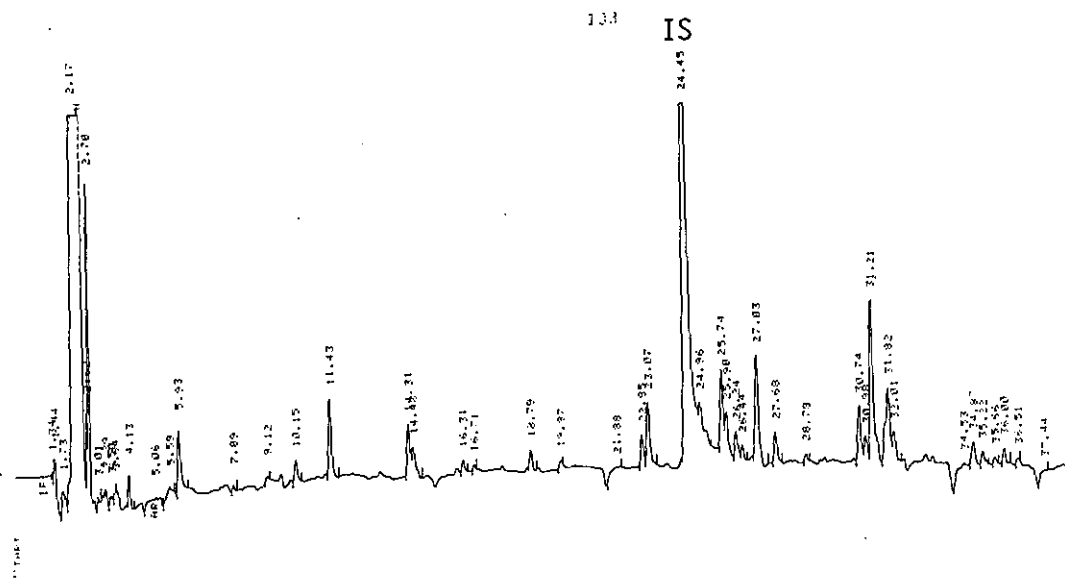


Figure 6. Electron capture gas chromatograms of extracts of water (top) and suspended matter (bottom) from Blair Waterway. IS = Internal Standard

A



B



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C

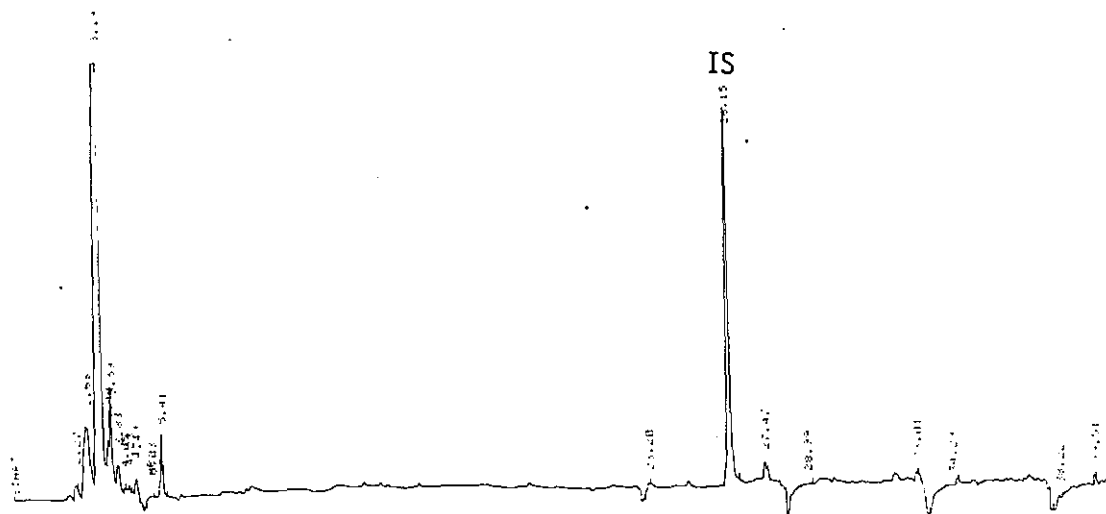
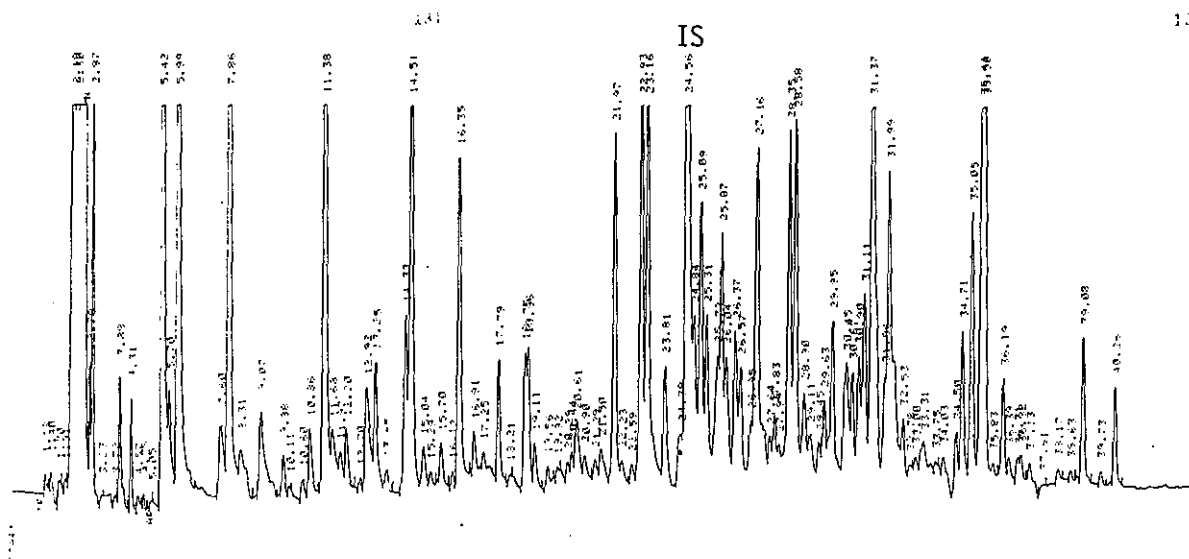
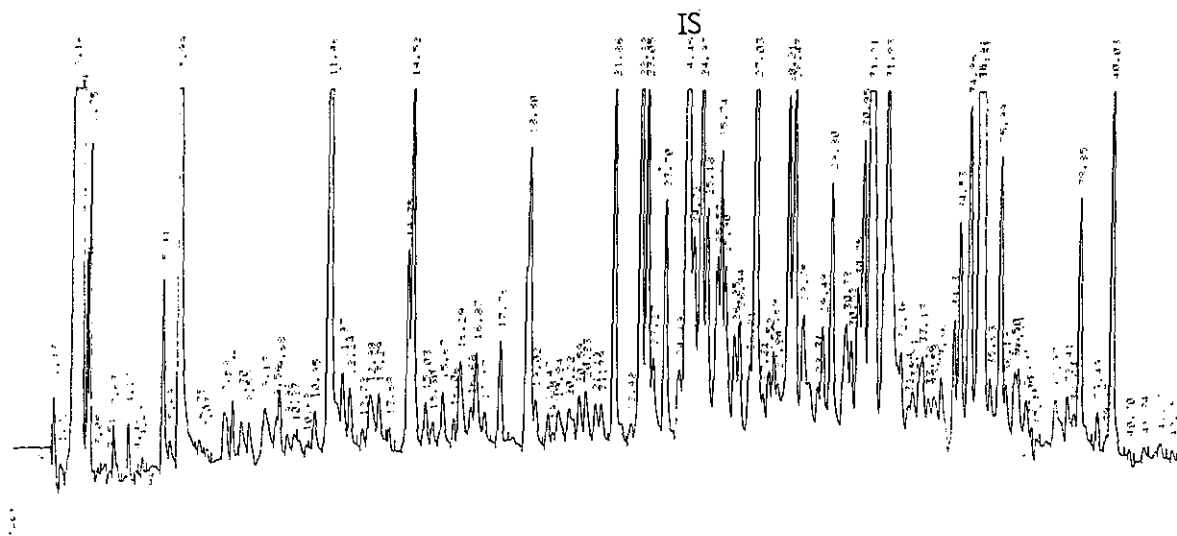


Figure 7. Electron capture gas chromatograms of extracts of water (top) and suspended matter (bottom) from Hylebos Waterway. IS = Internal Standard

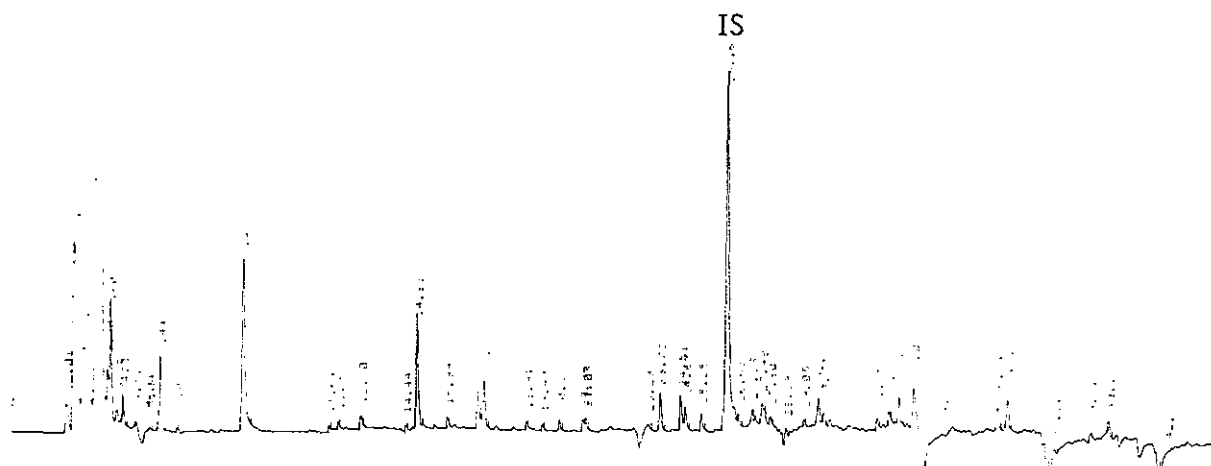
A



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C



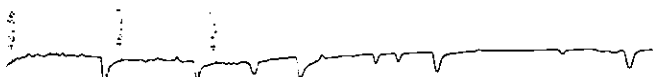
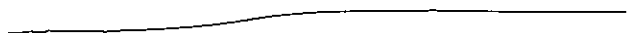


Figure 8. Electron capture gas chromatograms of halogenated compounds from extracts of water sampled from Blair Waterway in (A) July, (B) September and (C) November. IS = Internal Standard

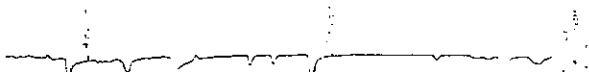
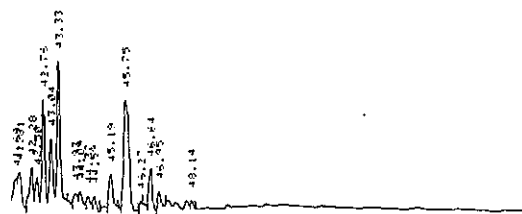


Figure 9. Electron capture gas chromatograms of halogenated compounds from extracts of water sampled from Hylebos Waterway in (A) July, (B) September and (C) November. IS = Internal Standard



1771



051

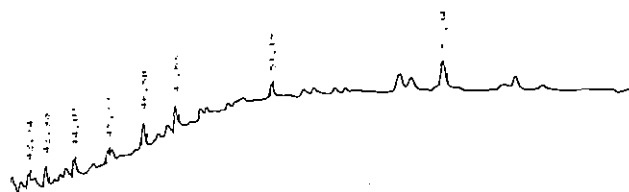


Figure 10. Electron capture gas chromatograms of halogenated compounds from extracts of suspended matter sampled from Blair Waterway in (A) July, (B) September, and (C) November. IS = Internal Standard

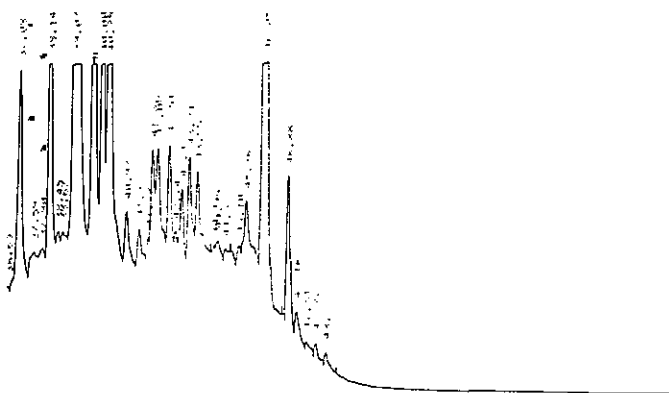
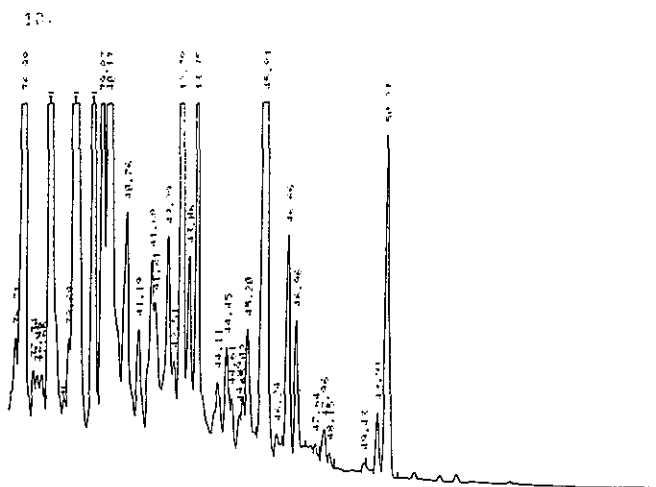
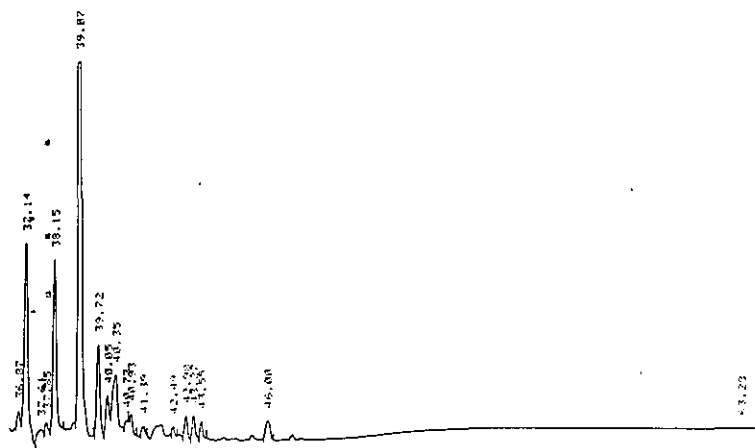
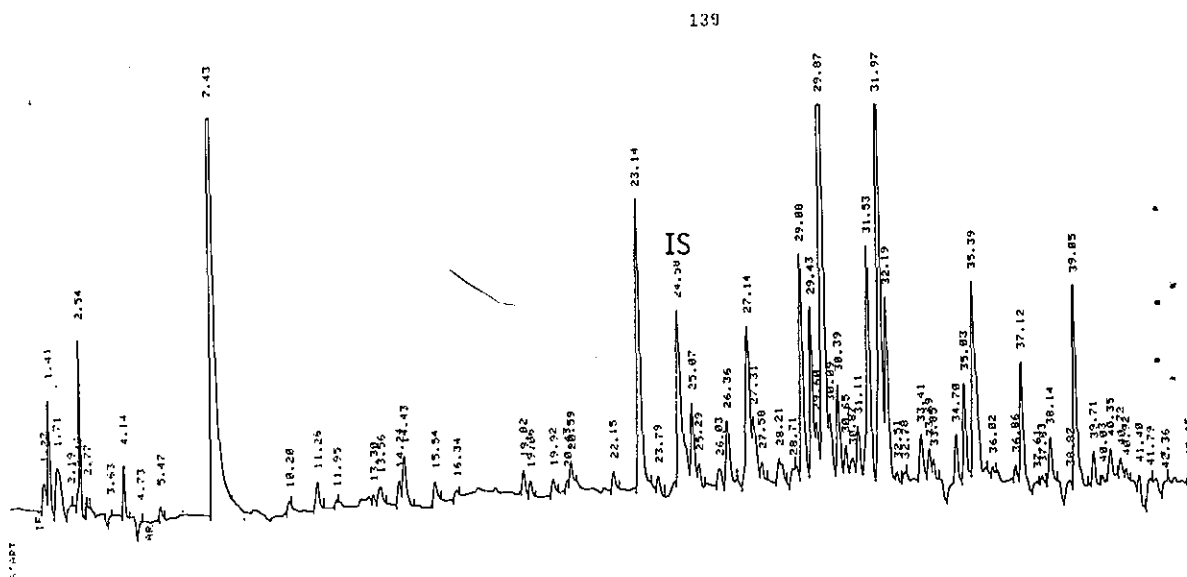
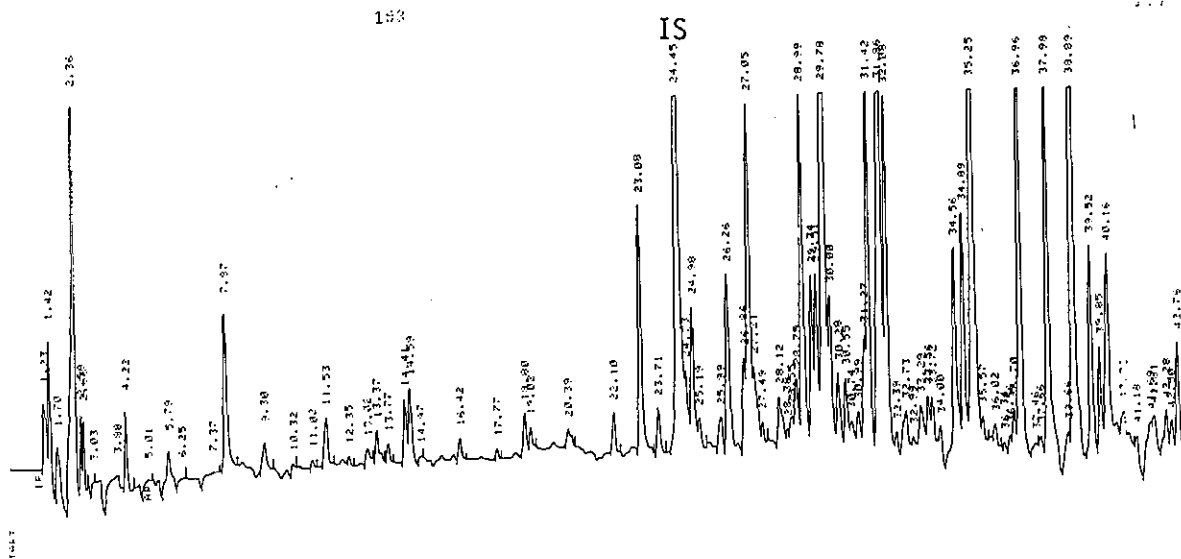


Figure 11. Electron capture gas chromatograms of halogenated compounds from suspended matter sampled from Hylebos Waterway in (A) July, (B) September and (C) November. IS = Internal Standard

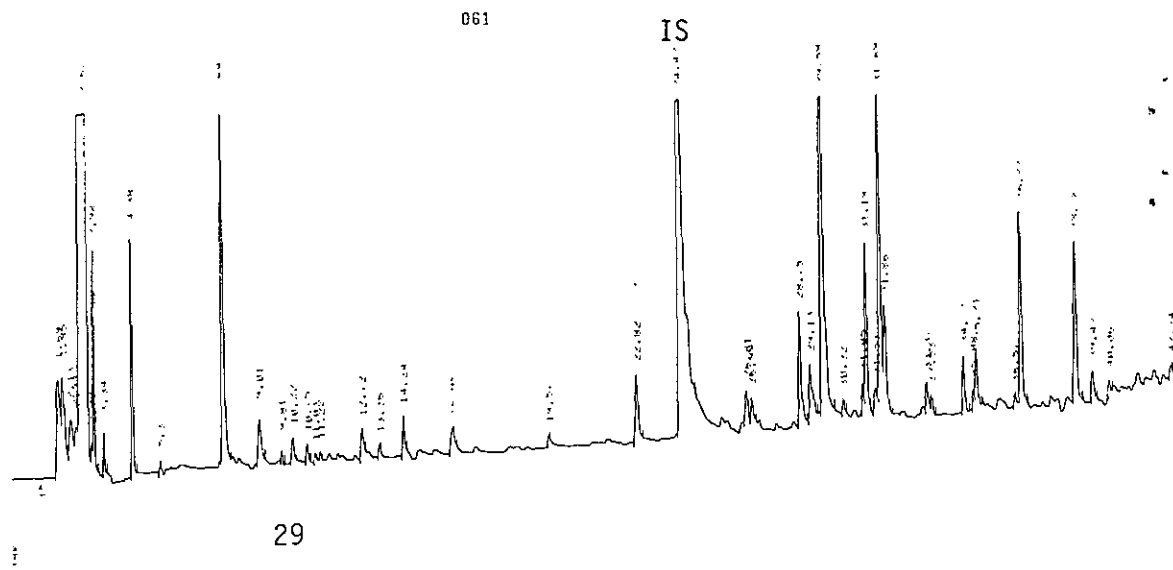
A



B



C



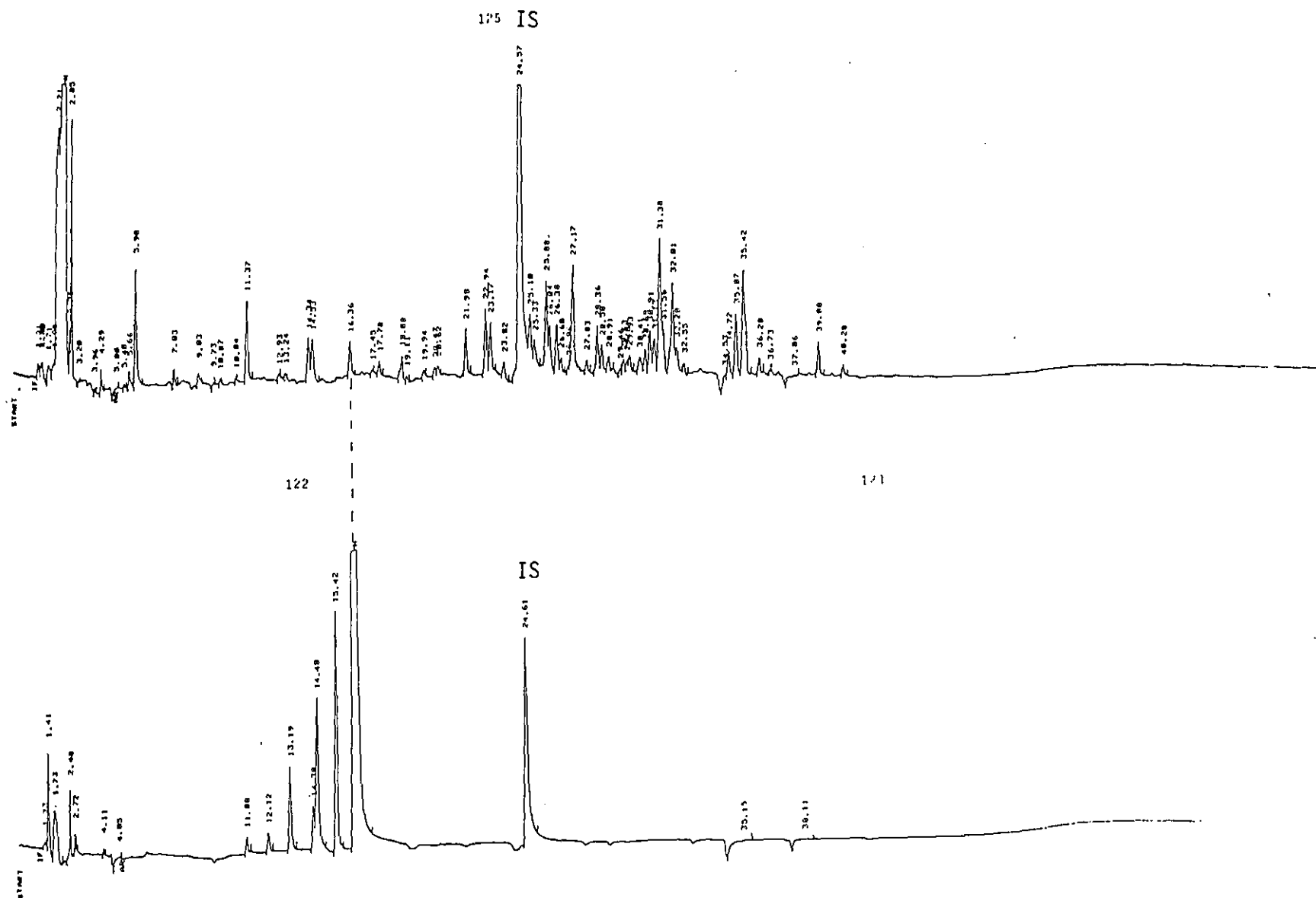
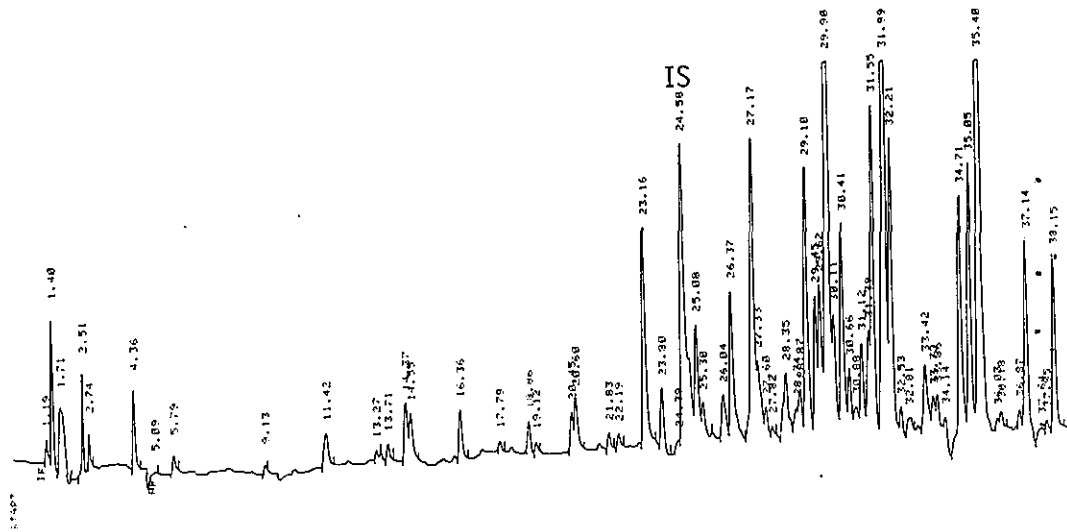
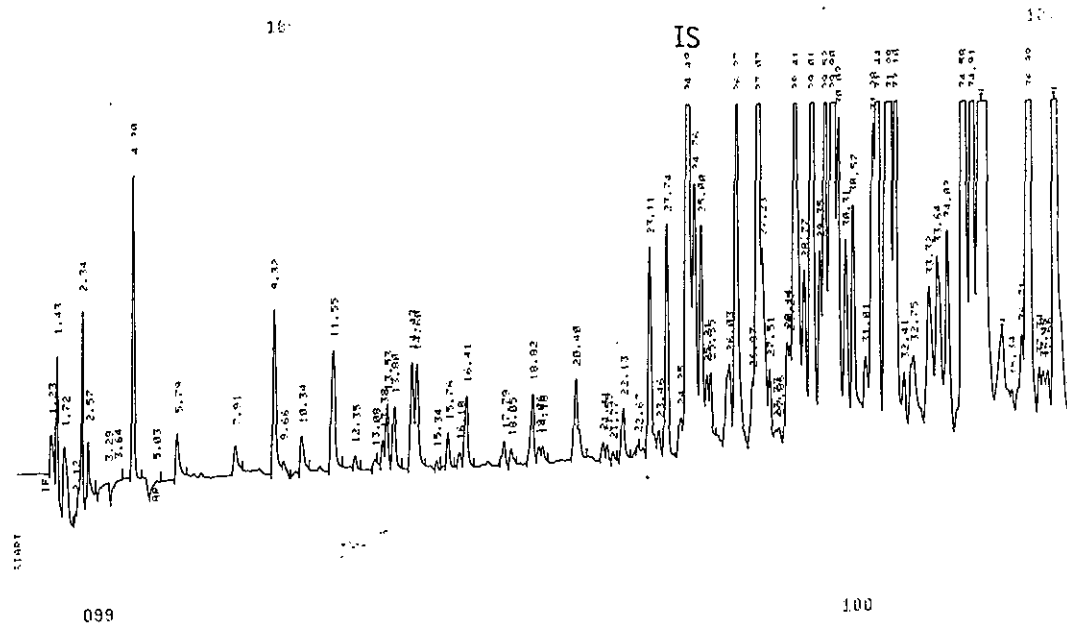


Figure 12. Electron capture gas chromatograms of an extract of water from Blair Waterway (top) and a synthetic standard of hexachloro-1,3-butadiene (bottom).
IS = Internal Standard

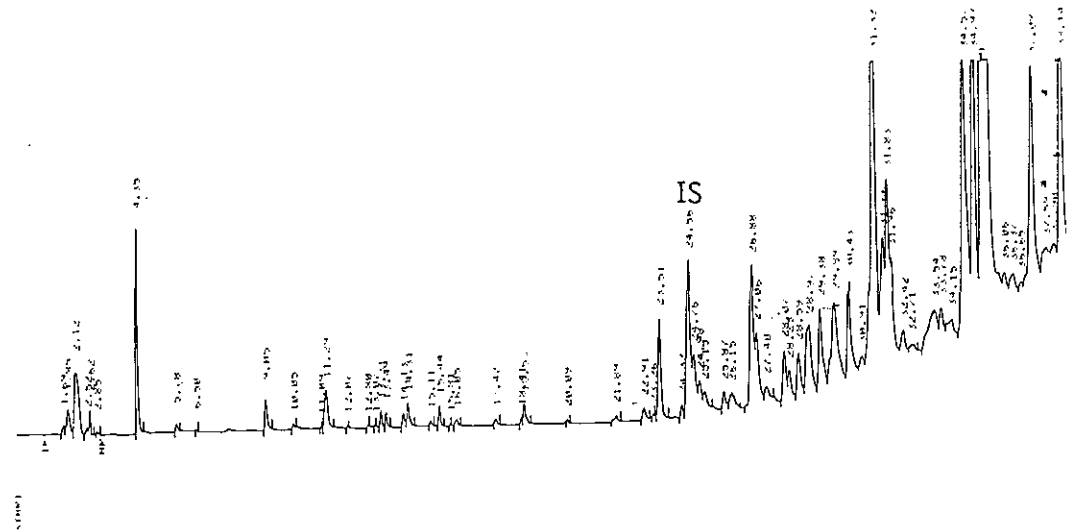
A



B



C



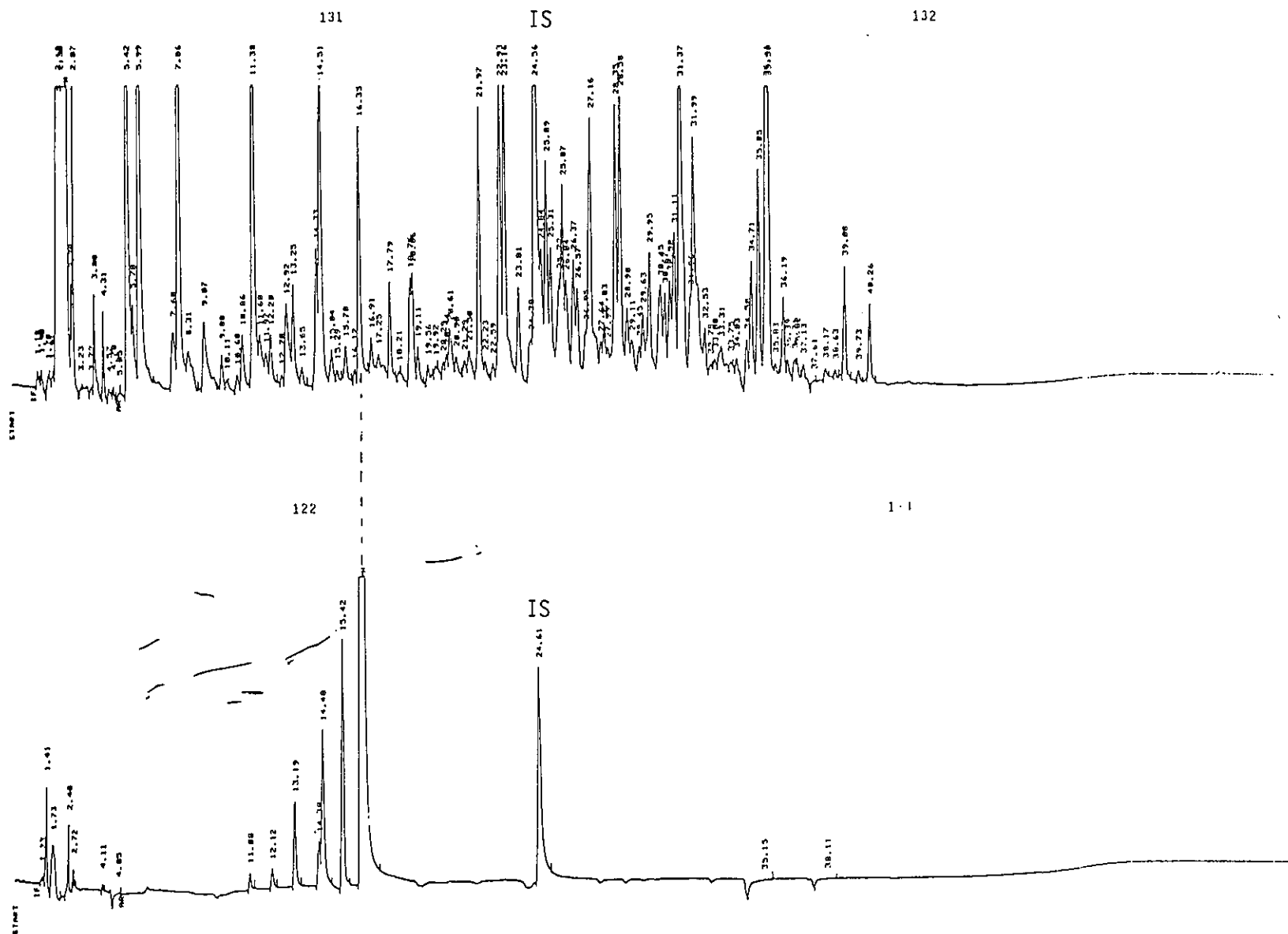


Figure 13. Electron capture gas chromatograms of an extract of water from Hylebos Waterway (top) and a synthetic standard of hexachloro-1,3-butadiene (bottom).
IS = Internal Standard

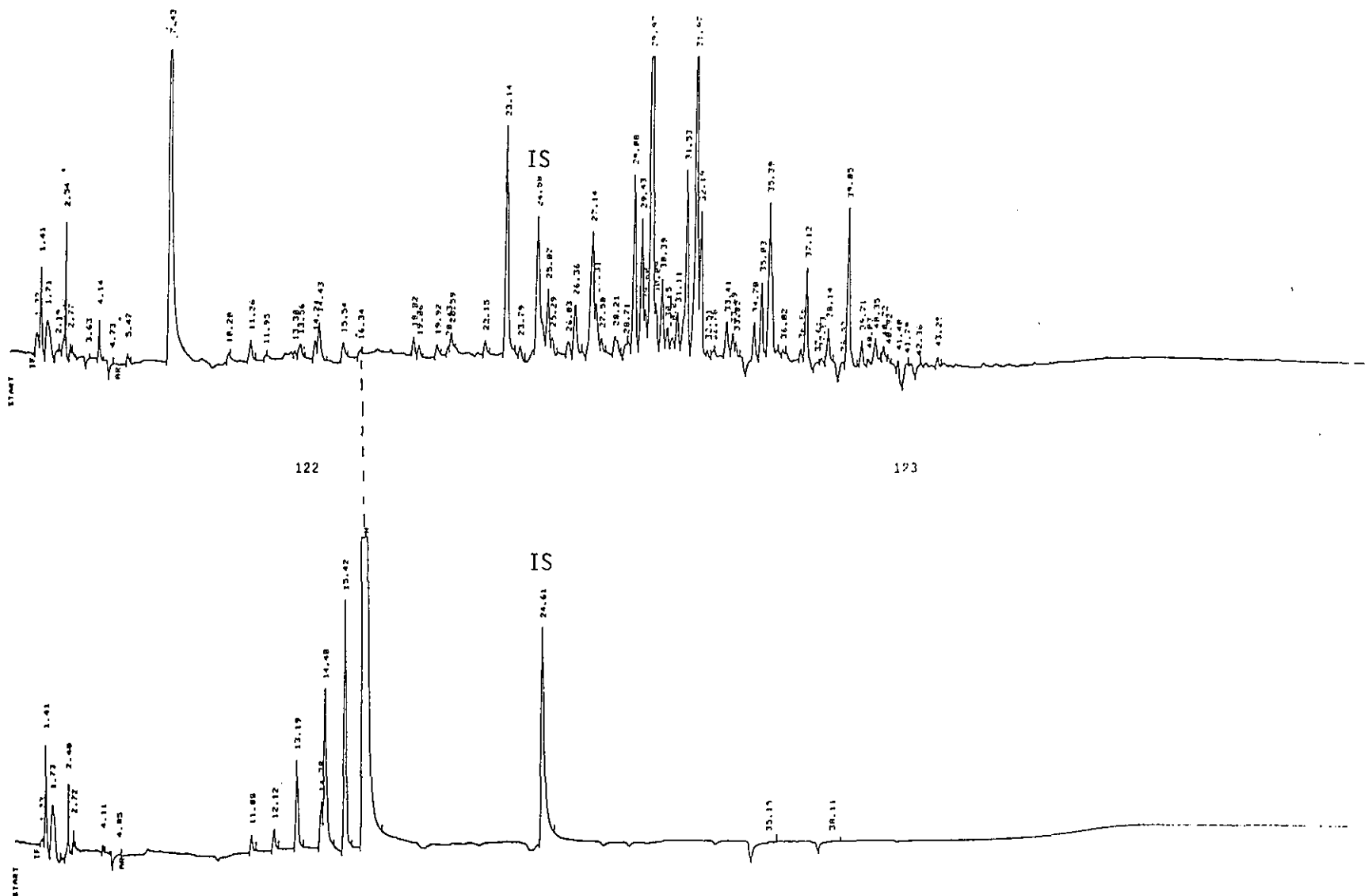


Figure 14. Electron capture gas chromatograms of and extract of suspended matter from Blair Waterway (top) and a synthetic standard of hexachloro-1,3-butadiene (bottom).
IS = Internal Standard

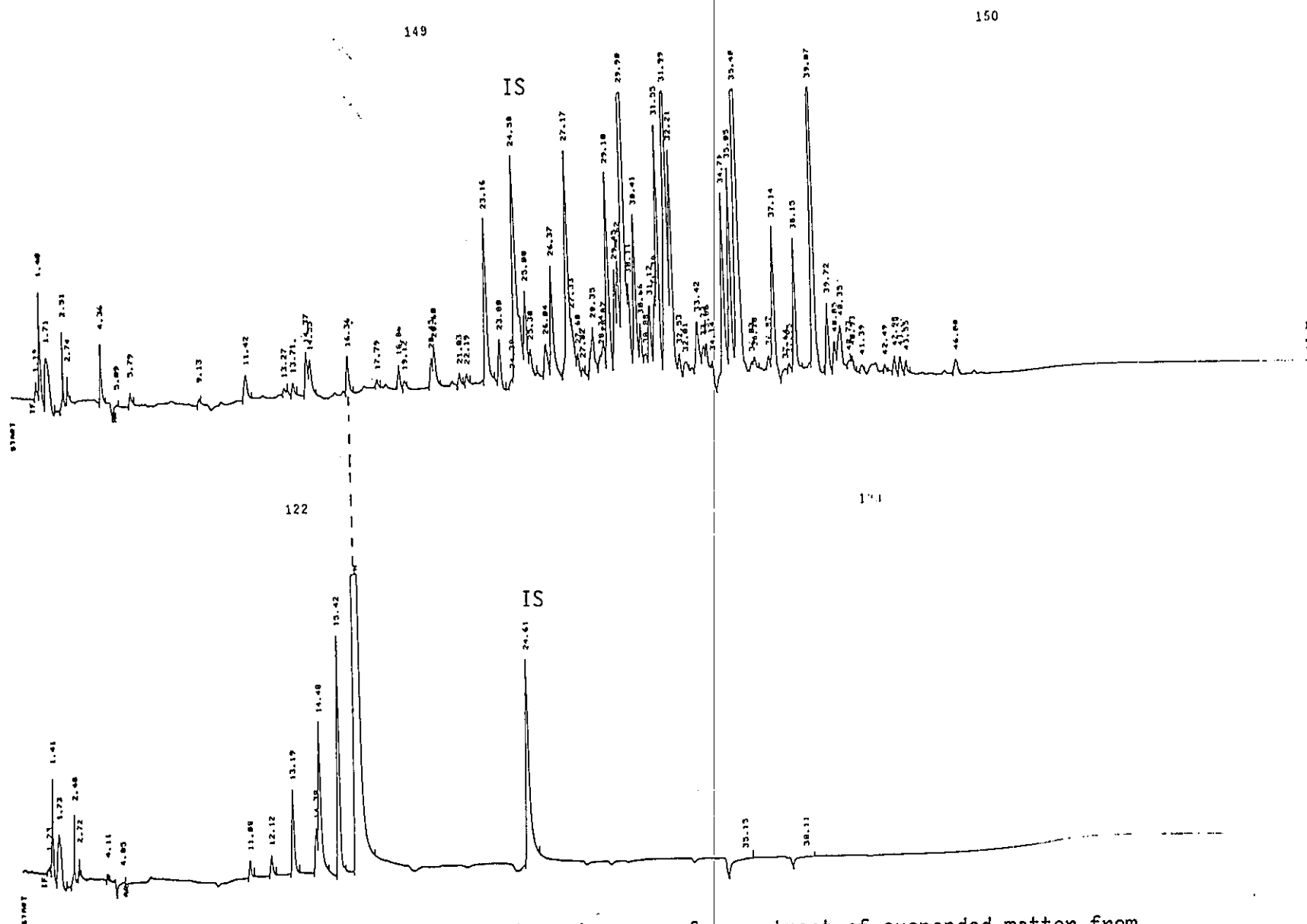
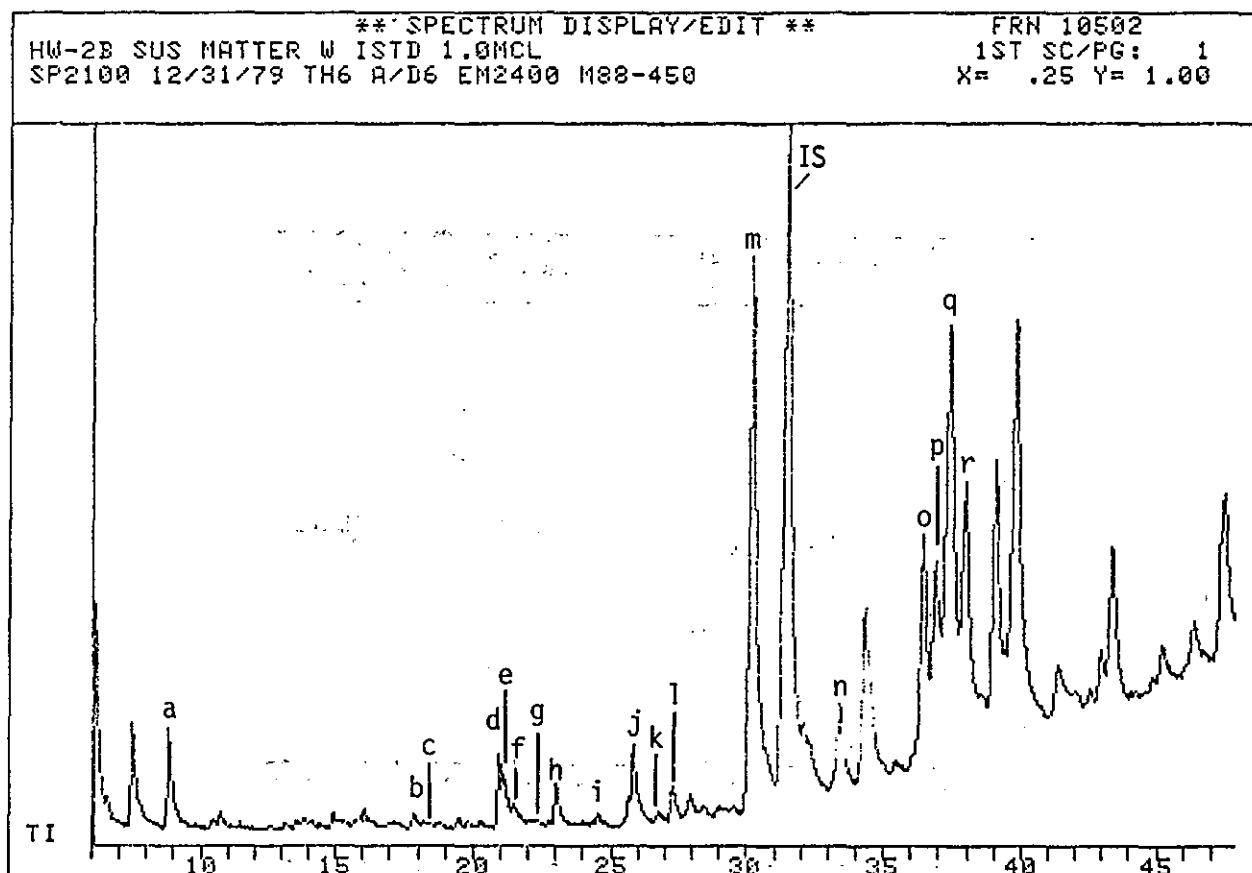


Figure 15. Electron capture gas chromatograms of an extract of suspended matter from Hylebos Waterway (top) and a synthetic standard of hexachloro-1,3-butadiene (bottom).
IS = Internal Standard



	Molecular Formula	Tentative Structural Assignments ¹		Molecular Formula	Tentative Structural Assignments ¹
a	C ₂ Cl ₄	tetrachloroethylene	l	C ₆ Cl ₄ H ₂	tetrachlorobenzene
b	C ₃ Cl ₅ H	pentachloropropene	m	C ₆ Cl ₆ H ₂	hexachlorocyclopentene, hexachloropentadiene
c	C ₄ Cl ₄ H ₂	tetrachlorobutadiene	n	C ₇ Cl ₆ H ₄	hexachloroheptatriene, hexachlorocycloheptadiene
d	C ₄ Cl ₅ H	pentachlorobutadiene		C ₆ Cl ₅ H	pentachlorobenzene
e	C ₆ Cl ₃ H ₃	trichlorobenzene	o	C ₆ Cl ₇ H	heptachlorocyclohexadiene, heptachlorohexatriene
f	C ₄ Cl ₅ H	pentachlorobutadiene	p	C ₆ Cl ₇ H	heptachlorocyclohexadiene, heptachlorohexatriene
g	C ₆ Cl ₃ H ₃	trichlorobenzene	q	C ₆ Cl ₇ H	heptachlorocyclohexadiene, heptachlorohexatriene
h	C ₄ Cl ₆	hexachlorobutadiene	r	C ₆ Cl ₆ H ₂	hexachlorocyclohexadiene, hexachlorohexatriene
i	C ₄ Cl ₆ H ₂	hexachlorobutene			
j	C ₅ Cl ₅ H ₃	pentachlorocyclopentene, pentachloropentadiene			
k	C ₆ Cl ₄ H ₂	tetrachlorobenzene			

¹ Except for hexachloro-1,3-butadiene and tetrachloroethylene all assignments of structure are tentative.

Figure 16. Total ion mass chromatograms of halogenated compounds tentatively identified in extract of suspended matter from Hylebos Waterway. IS = Internal Standard

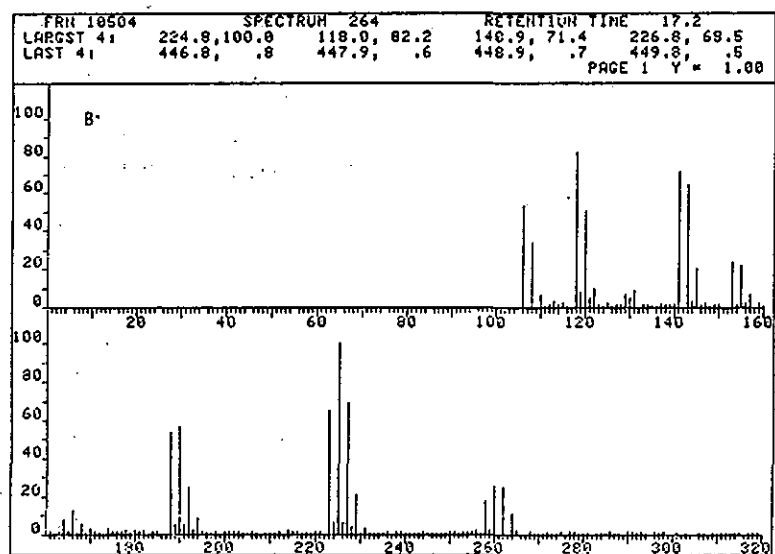
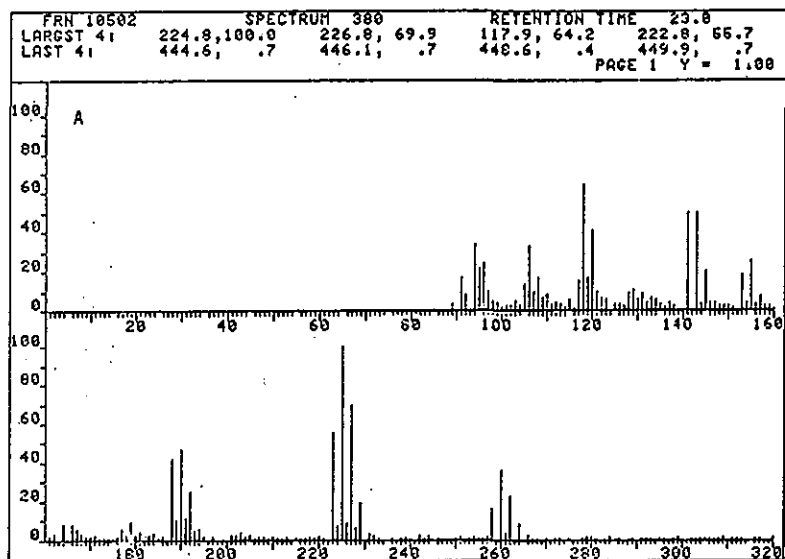
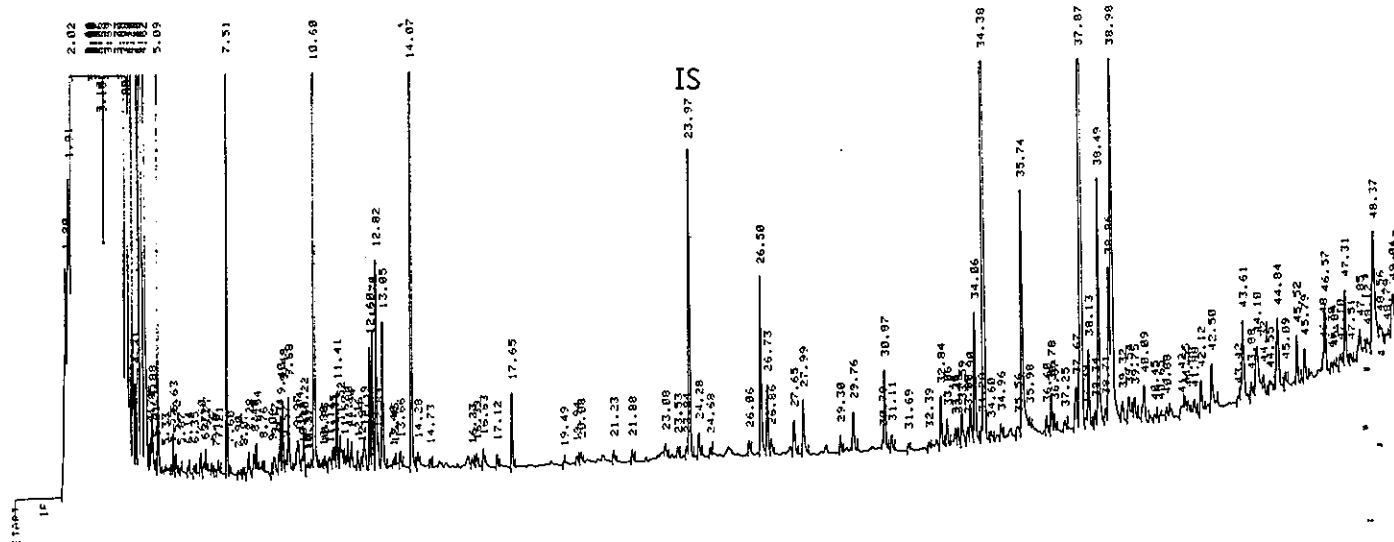
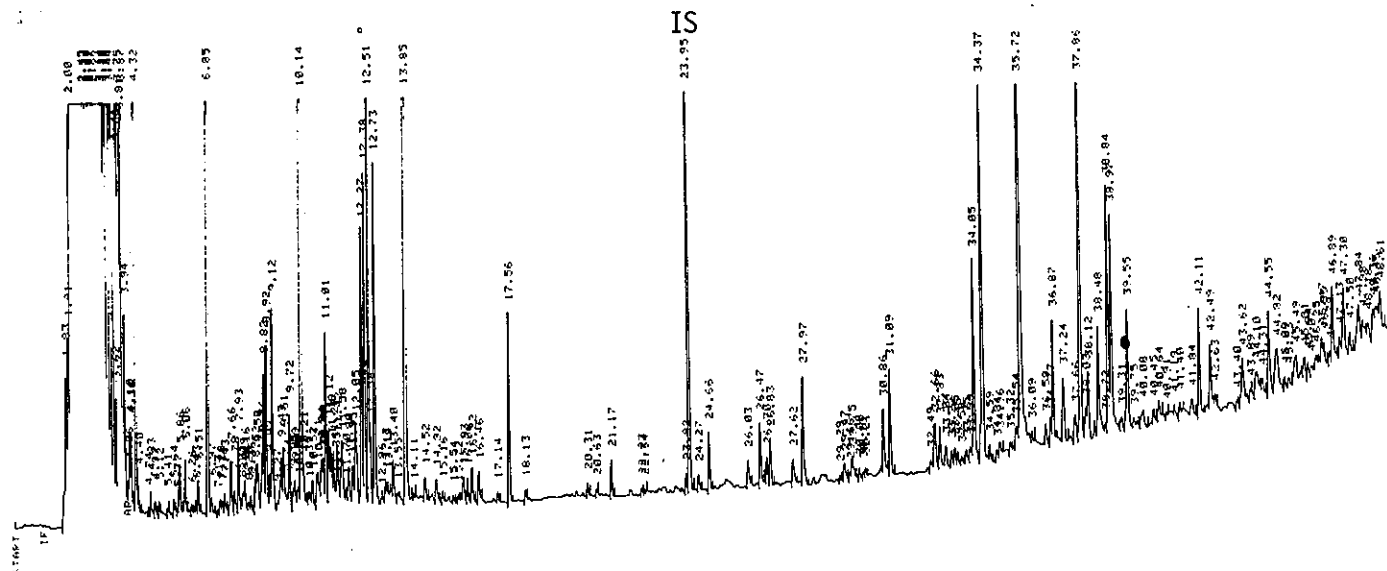


Figure 17. Mass spectra of (A) hexachloro-1,3-butadiene isolated from suspended matter of Hylebos Waterway and (B) hexachloro-1,3-butadiene analytical standard.

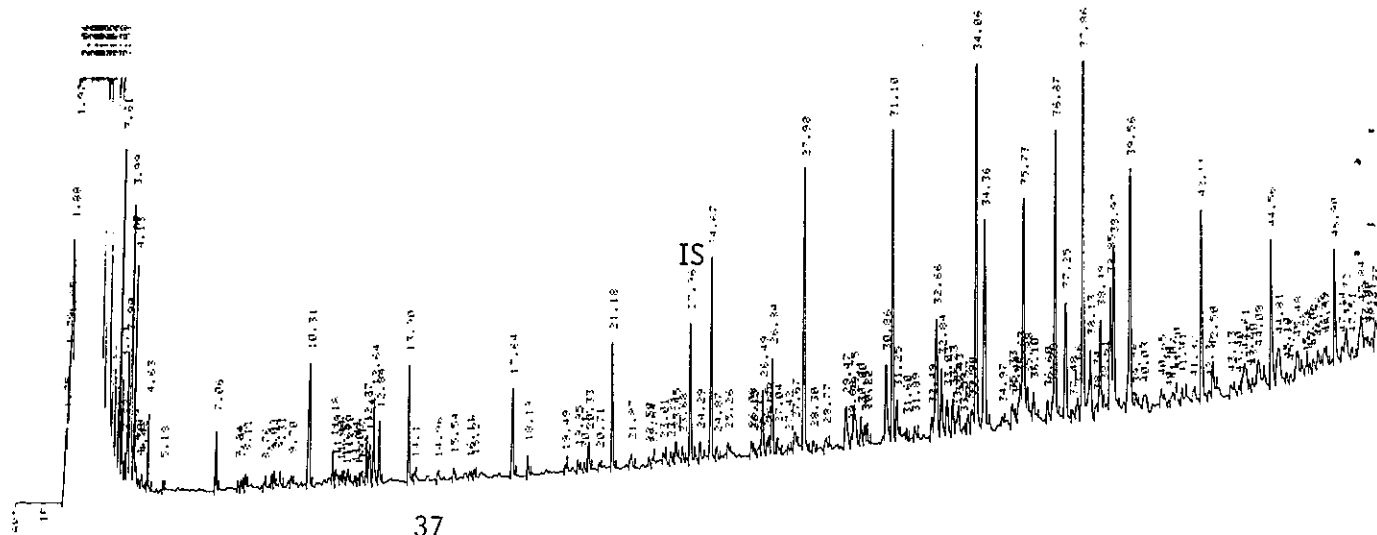
A



B



C



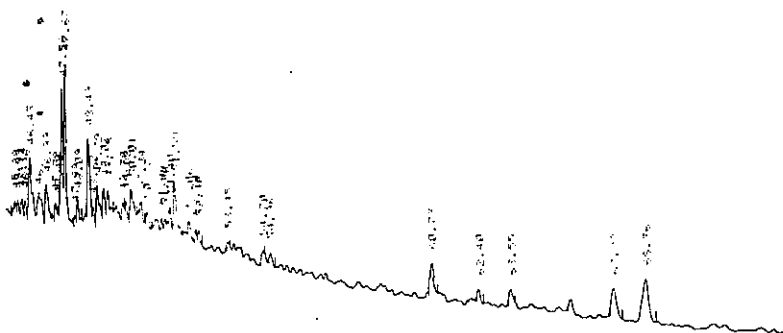
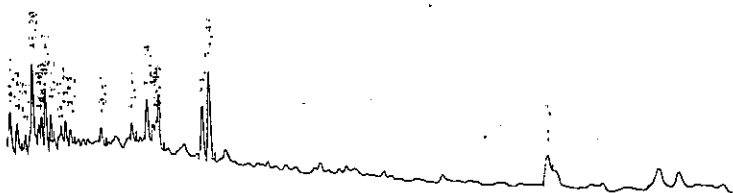


Figure 19. GC chromatograms showing typical variation in aromatic hydrocarbon composition of suspended matter in Puget Sound. (A) Port Madison, (B) Pier 54, and (C) Hylebos Waterway. IS = Internal Standard



1.2

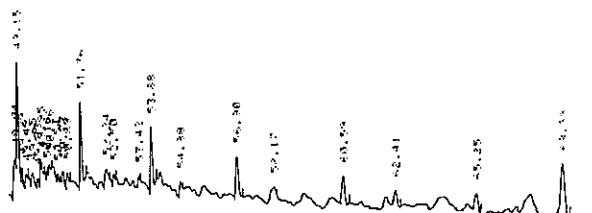
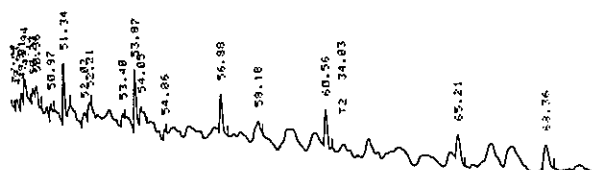
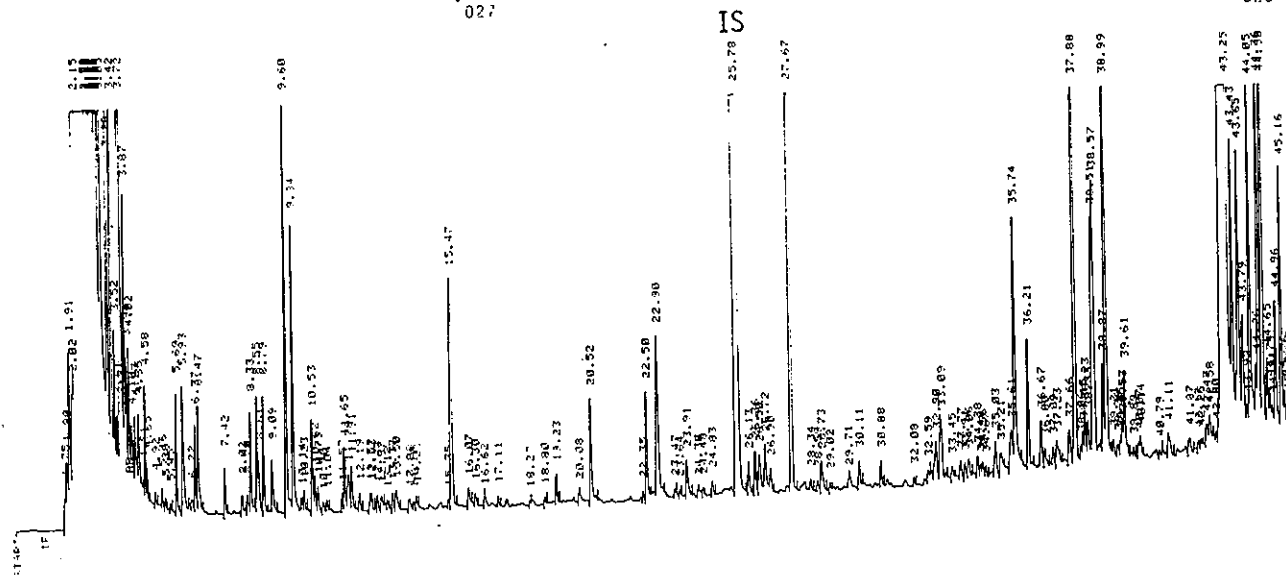
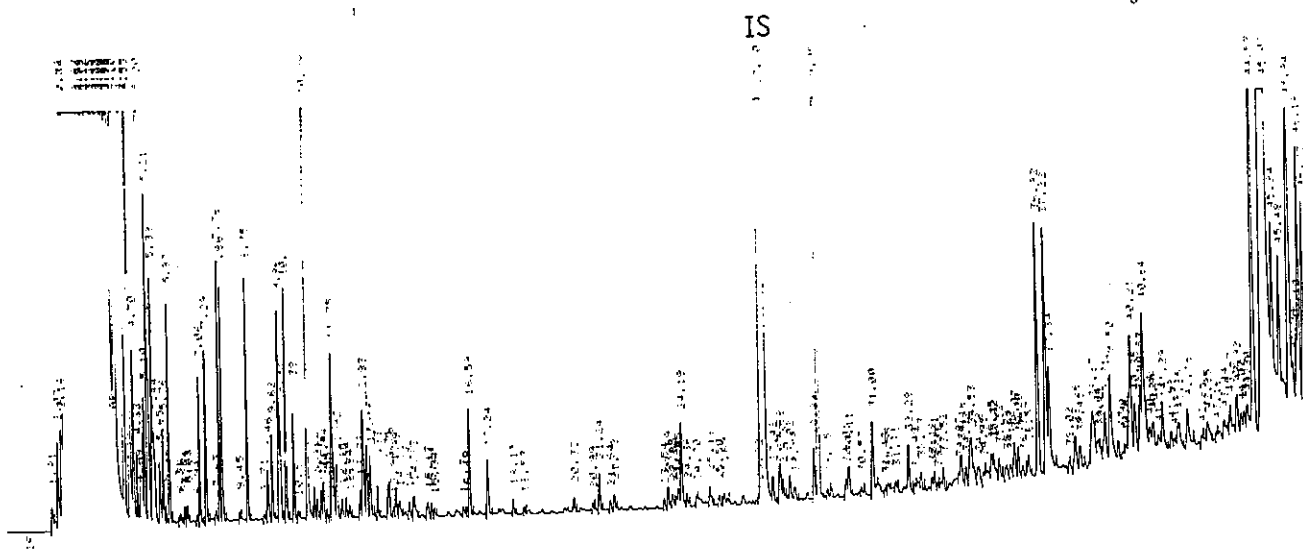


Figure 18. GC chromatograms showing typical variation in saturate hydrocarbon composition of suspended matter in Puget Sound. (A) Port Madison, (B) Pier 54, and (C) Hylebos Waterway. IS = Internal Standard

A



B



C

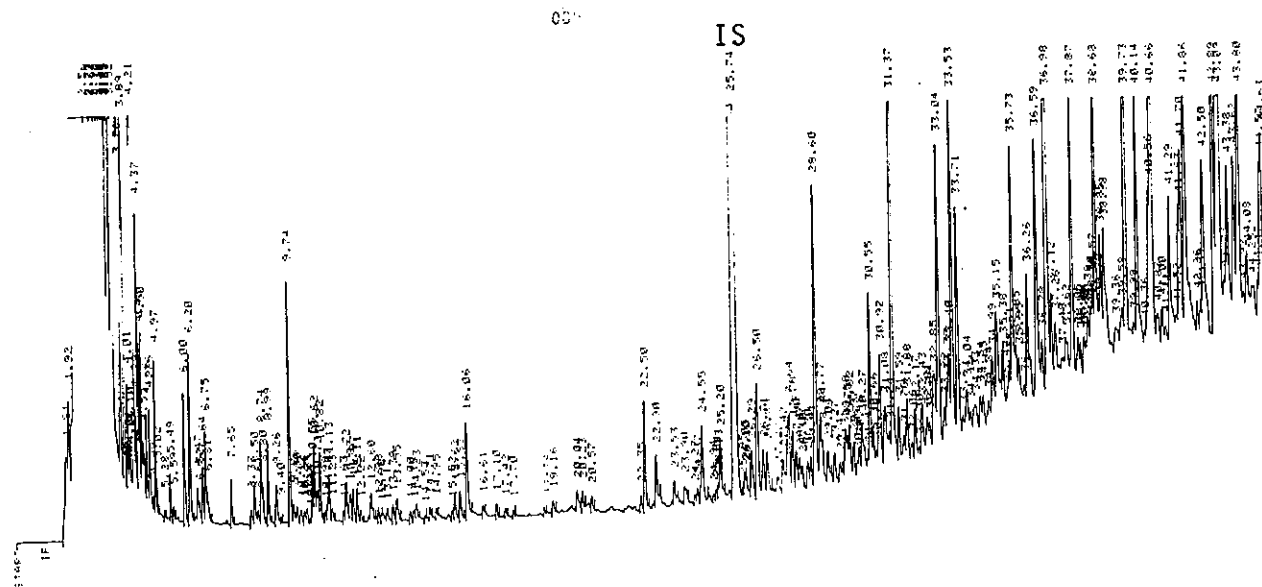


Table 1. Physical and Chemical Parameters for Puget Sound Stations

JULY DATA

Station Location	Sample Depth(m)	Temperature C°	Salinity ‰	DO (ppm)	Suspended Load mg/ℓ dry wt	% Organic C ¹ (dry wt)	DOC ² mgC/ℓ	POC ³ mgC/ℓ	Chlorophyll A mg/m ³
Seattle, Pier 54	2	15°	28.9	10	2.2	10	1.2	0.22	2.3
Seattle, Harbor Island	2	15°	26.3	10	4.0	4.3	1.1	0.17	6.6
Seattle, West Waterway	2	14°	28.0	10	4.4	4.3	1.3	0.19	2.0
Sinclair Inlet, Bremerton	3	16°	29.4	10	2.7	3.0	1.2	0.08	1.4
Tacoma, Puyallup River	0.5	17°	8.3	9	29	1.2	2.2	0.36	2.5
Tacoma, Hylebos Waterway	2	16°	26.8	9	4.7	6.0	1.2	0.28	3.4
Tacoma, Blair Waterway	2	14°	25.7	11	6.4	6.7	1.1	0.43	2.2
Olympia, Budd Inlet	2	16°	29.0	17	8.6	12	1.6	1.0	12.8
Port Madison	2	15°	29.2	11	1.4	13	1.1	0.18	0.8

¹% organic carbon (dry wt) content of suspended matter²DOC = dissolved organic carbon³POC = particulate organic carbon

Table 1. (continued)

SEPTEMBER DATA

Station Location	Sample Depth(m)	Temperature C°	Salinity ‰	DO (ppm)	Suspended Load mg/ℓ dry wt	% Organic C (dry wt)	DOC mgC/ℓ	POC mgC/ℓ	Chlorophyll A mg/m ³
Tacoma, Hylebos Waterway	2	17°	28.4	11	4.1	5.6	1.2	0.23	0.9
Tacoma, Blair Waterway	2	16°	29.8	15	2.6	5.0	1.1	0.31	2.4

NOVEMBER DATA

Station Location	Sample Depth(m)	Temperature C°	Salinity ‰	DO (ppm)	Suspended Load mg/ℓ dry wt	% Organic C (dry wt)	DOC mgC/ℓ	POC mgC/ℓ	Chlorophyll A mg/m ³
Tacoma, Hylebos Waterway	2	11°	30.0	8	2.5	4.0	0.90	0.10	0.3
Tacoma, Blair Waterway	2	10°	30.3	8	1.9	5.3	1.25	0.10	0.3

Table 2. Concentration of Elements in Puget Sound Suspended Matter Collected July 1979 ppm Dry Weight
(mean values from duplicate samples, uncertainties of approximately $\pm 20\%$ for σ)

ELEMENT	Pier 54	Harbor Island	West Waterway	Puyallup River	Hylebos Waterway	Blair Waterway	Bremerton	Olympia	Port Madison
As	<22	37	44	<22	94	52	31	<22	28
Br	58	78	75	179	303	95	126	34	214
Co	8.5	7.5	14	2.5	8.8	8.2	7.4	2.2	6.4
Cr	79	52	88	26	66	54	80	24	60
Cu	230	179	208	156	226	156	130	47	68
Eu	0.39	0.52	0.94	0.22	0.68	0.68	0.41	0.11	0.28
Mn	1850	1050	1090	373	581	660	1730	146	2090
Ni	82	39	44	47	55	28	58	12	55
Pb	380	338	448	153	250	111	146	26	97
Rb	27	33	39	25	18	37	24	8	<20
Sb	2.9	3.8	9.8	0.7	9.0	4.7	3.5	0.4	1.0
Se	2.3	1.1	1.2	0.5	1.6	1.2	1.7	1.5	1.8
Sr	205	213	213	262	370	328	<200	<200	<200
V	51	62	106	22	80	59	53	22	36
Zn	900	540	580	360	380	340	490	180	280

Table 3. Concentration of Elements in Puget Sound Suspended Matter Collected July 1979 % Dry Weight
(mean values from duplicate samples, uncertainties of approximately $\pm 20\%$ for σ)

ELEMENT	Pier 54	Harbor Island	West Waterway	Puyallup River	Hylebos Waterway	Blair Waterway	Bremerton	Olympia	Port Madison
Al	3.7	7.1	6.6	6.3	8.1	6.1	4.2	0.2	1.4
Ca	0.7	1.6	1.5	2.3	2.2	2.6	1.4	0.6	0.8
Cl	0.30	0.83	0.43	4.8	0.74	1.2	1.5	0.53	2.9
Fe	4.0	5.9	5.4	1.9	3.9	3.3	2.8	0.5	1.4
K	0.33	0.78	0.76	0.86	0.89	0.86	0.52	0.15	0.37
P	0.75	1.0	0.59	0.66	0.62	0.67	0.67	0.48	0.72
S	0.55	0.38	0.30	0.49	0.44	0.54	0.55	0.53	0.66
Si	15	22	20	18	25	28	19	2	11
Ti	0.16	0.33	0.36	0.32	0.30	0.38	0.45	0.04	0.15

Table 4. Concentration of Elements in Puget Sound Suspended Matter Collected During September and November, 1979 ppm Dry Weight (mean values from duplicate samples, uncertainties of approximately $\pm 20\%$ for σ)

ELEMENT	JULY 1979		SEPTEMBER 1979		NOVEMBER 1979	
	Hylebos Waterway	Blair Waterway	Hylebos Waterway	Blair Waterway	Hylebos Waterway	Blair Waterway
As	94	52	65	42	86	106
Br	303	95	258	250	112	163
Co	8.8	8.2	10.2	7.7	8.4	7.9
Cr	66	54	104	63	61	65
Cu	226	156	290	303	189	484
Eu	0.68	0.68	0.82	0.62	0.71	0.66
Mn	581	660	761	686	741	654
Ni	55	28	44	45	51	32
Pb	250	111	237	139	181	396
Rb	18	37	31	26	31	34
Sb	9.0	4.7	4.6	4.4	6.3	9.2
Se	1.6	1.2	1.2	1.5	1.3	1.5
Sr	370	328	440	373	369	409
V	80	59	86	77	83	89
Zn	380	340	328	335	191	640

Table 5. Concentration of Elements in Puget Sound Suspended Matter Collected During September and November, 1979 % Dry Weight (mean values from duplicate samples, uncertainties of approximately $\pm 20\%$ for σ)

ELEMENT	<u>JULY 1979</u>		<u>SEPTEMBER 1979</u>		<u>NOVEMBER 1979</u>	
	Hylebos Waterway	Blair Waterway	Hylebos Waterway	Blair Waterway	Hylebos Waterway	Blair Waterway
Al	8.1	6.1	6.5	4.8	5.5	4.9
Ca	2.2	2.6	2.6	2.5	2.2	2.7
Cl	0.74	1.2	2.2	2.1	0.34	2.8
Fe	3.9	3.3	3.5	3.2	3.9	5.4
K	0.89	0.86	0.90	0.80	0.90	0.99
P	0.62	0.67	0.63	0.75	0.43	0.94
S	0.44	0.54	0.62	0.47	0.31	0.49
Si	25	28	23	22	23	25
Ti	0.30	0.38	0.29	0.24	0.29	0.32

Table 6. Elemental Intercomparison of Puget Sound Sediments. Values in ppm Dry Weight

ELEMENT	COMMENCEMENT BAY Mesa Station #09028		DUWAMISH WATERWAY Mesa Station # 10031		CASE INLET Mesa Station # 12063	
	BNW	NMFS	BNW	NMFS	BNW	NMFS
Al	70400	13060	80100	>20000	52800	6430
As	38	0	36	95	3.4	0
Ca	57000	>200000	20000	9000	16000	9600
Cr	90	34	94	45	90	21
Cu	99	85	127	131	12	10
Fe	45000	24000	53000	46000	13000	11000
Ga	18	51	21	65	9	34
K	11000	89	13000	220	8100	44
Mn	570	202	590	416	330	192
Na	26300	12846	23000	15823	19500	4935
Ni	56	42	31	36	19	19
Pb	141	111	316	265	11	7.9
Sb	5.0	43	8.7	74	1.2	19
Se	1.4	27	<1.3	80	<1.0	11
Si	210000	149	240000	101	390000	143
Sr	820	513	320	124	270	26
Ti	3900	940	5000	1600	1700	6800
V	130	67	147	96	57	28
Zn	156	134	227	204	25	23

Table 7. Concentrations and Distributions of Hexachloro-1,3-butadiene in Suspended Matter and Water from Blair Waterway and Hylebos Waterway. Concentrations Expressed in ng/liter (pptr) for Water and ng/g (ppb) Dry Weight for Suspended Matter.

Sampling Time	Concentrations ¹				Distributions ³			
	Blair Waterway Sus. Matter	Blair Waterway Water	Hylebos Waterway Sus. Matter	Hylebos Waterway Water	Blair Waterway Sus. Matter	Blair Waterway Water	Hylebos Waterway Sus. Matter	Hylebos Waterway Water
Jul. 1979	1.0 ± 0.5	0.6 ± 0.0	56.4 ± 41.3	2.4 ± 1.0	0	100	10	90
Sep. 1979	3.0 ± 1.1	0.2, <0.1	147.5 ± 5.5	0.3 ± 0.2	2	98	70	30
Nov. 1979	1.5 ± 0.5	<0.1, <0.1	9.9 ± 6.4	0.2, ²	2	98	15	85

¹Duplicate samples analyzed and reported as $\bar{x} \pm \overline{SE}$, n = 2. XAD-2 water values not corrected for recovery, however, a recovery of 47% has recently been reported (Rossum and Webb, 1978).

²Only one sample analyzed.

³Relative concentrations between suspended matter and water base on one liter of water. Example, Hylebos Waterway, July 1979. Amount of hexachloro-1,3-butadiene in water = 2.4 ng. Amount of hexachloro-1,3-butadiene associated with suspended matter in one liter of water =

$$\frac{56.4 \text{ ng}}{1000 \text{ mg}} \times \frac{4.7 \text{ mg}}{1 \text{ liter}} = 0.27 \text{ ng} \quad \% \text{ on suspended matter} = \frac{0.27}{2.4 + 0.27} \times 100 = 10 \quad \% \text{ in water} = \frac{2.4}{2.4 + 0.27} = 90$$

Table 8. Characterized and Quantitated Purgable Organic Compounds in Waters from Puget Sound as a Function of Sampling Location and Season. (Concentrations in $\mu\text{g}/\ell$, ppb)

	July 1979								September 1979			November 1979			
	HI	WW	PR	OLY	BRE	PM	BW	HW	BW	HW	HW	BW	BW	HW	HW
Carbon disulfide	(1) +	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Methylene chloride	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	109.4	<2.5	30.2	22.0	34.3	6.8	38.8	6.2	3.8
1,2-Dichloroethylene	<0.6	<0.6	(3) <0.6?	<0.6	(2) n.d.	n.d.	n.d.	1.0	n.d.	1.5	2.4	n.d.	<0.3?	1.1	0.8
Trichloroethylene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1?	0.8	<0.1	1.8	3.0	n.d.	n.d.	1.8	1.4
Tetrachloroethylene	<0.1	<0.1	<0.1	n.d.	n.d.	<0.1	<0.3?	<0.2	<0.3?	0.4	0.3	<0.3?	<0.3?	<0.3	<0.3
Chlorodibromomethane	<0.1?	<0.1?	<0.1?	n.d.	n.d.	n.d.	n.d.	<0.1	n.d.	0.2	<0.2	n.d.	n.d.	<0.2	<0.2
Bromoform	<0.2?	<0.2?	<0.2?	n.d.	n.d.	n.d.	n.d.	1.1	n.d.	1.2	0.7	n.d.	n.d.	<0.7	<0.7

¹Present, but not quantified (believed to be artifact of sampling apparatus).

²n.d. = not detected.

³A question mark indicates a tentative identification only (see appendix on analytical procedures for criteria for the identification of purgable organic compounds).

Table 9. Concentrations of Saturate Hydrocarbons in Filtered Water from Nine Sampling Sites in Puget Sound, $\bar{x} \pm \text{SE}$, Parts Per Trillion (pptr)

Compound	Seattle P-54 ²	Seattle ¹ HI	Seattle WW	Bremerton SI	Tacoma PR	Tacoma HW	Tacoma BW	Olympia BI	Port Madison
C ₁₃	<3	<3	<3	<3	<3	<3	<3	<4	<3
C ₁₄	<3	<3	<3	<3	<3	<3	<3	<4	<3
C ₁₅	<3	<3	<2	<3	<3	<3	<3	<3	<3
C ₁₆	<2	<3	<2	<3	<3	<2	<3	<3	<3
C ₁₇	<2	<3	<2	<3	<2	<2	<3	<3	<3
Pristane	<2	<3	<2	<3	<2	<2	<3	<3	<3
C ₁₈	<2	<3	<2	<3	<2	<2	<2	<3	<3
Phytane	<2	<3	<2	<2	<2	<2	<2	<3	<3
C ₁₉	<2	<3	<2	<2	<2	<2	<2	<3	<3
C ₂₀	<2	<2	<2	<2	<2	<2	<2	<3	<2
C ₂₁	<2	<3	<2	<3	<2	<2	<2	<3	<3
C ₂₂ ³	9 \pm 2	18	15 \pm 13	14 \pm 11	10 \pm 0	<2	11 \pm 6	<3	4 \pm 2
C ₂₃ ³	<14	52	39 \pm 31	37 \pm 22	18 \pm 19	<3	32 \pm 25	7 \pm 6	11 \pm 12
C ₂₄ ³	64 \pm 11	109	84 \pm 62	84 \pm 81	68 \pm 6	6 \pm 6	66 \pm 64	14 \pm 16	26 \pm 33
TOTAL	86 \pm 5	179	138 \pm 106	135 \pm 78	91 \pm 10	6 \pm 6	110 \pm 95	19 \pm 26	38 \pm 53

¹Only one sample analyzed.

²P-54 = Pier 54, HI = Harbor Island, WW = West Waterway, SI = Sinclair Inlet, PR = Puyallup River, HW = Hylebos Waterway, BW = Blair Waterway, BI = Budd Inlet

³High concentrations are a result of septum bleed contamination.

Table 10. Seasonal Variation in the Concentrations of Saturate Hydrocarbons from Filtered Water from Hylebos Waterway (Tacoma) and Blair Waterway (Tacoma), $\bar{x} \pm SE$, Parts Per Trillion (pptr)

Compound	Hybelos Waterway			Blair Waterway		
	Jul 1979	Sep 1979	Nov 1979	Jul 1979	Sep 1979	Nov 1979
C ₁₃	<3	<0.2	<1	<3	<0.2	<1
C ₁₄	<3	<0.2	<1	<3	<0.2	<1
C ₁₅	<3	<0.2	<1	<3	<0.2	<1
C ₁₆	<2	<0.2	<1	<3	<0.2	<1
C ₁₇	<2	<0.2	<1	<3	<0.2	<1
Pristane	<2	<0.2	<1	<3	<0.2	<1
C ₁₈	<2	<0.2	<1	<2	<0.2	<1
Phytane	<2	<0.2	<1	<2	<0.2	<1
C ₁₉	<2	<0.2	<1	<2	<0.2	<1
C ₂₀	<2	<0.2	<1	<2	<0.2	<1
C ₂₁	<2	<0.2	<1	<2	<0.2	2 \pm 3
C ₂₂ *	<2	<0.2	7	11 \pm 6	<0.2	4 \pm 6
C ₂₃ *	<3	<0.2	1	32 \pm 25	<0.2	5 \pm 6
C ₂₄ *	6 \pm 6	<0.2	1	66 \pm 64	<0.2	5 \pm 6
TOTAL	6 \pm 6	--	9	110 \pm 95	--	15 \pm 21

¹Higher concentrations (Hylebos Waterway, July 1979; Blair Waterway, July 1979, November 1979) are a result of septum bleed.

Table 11. Concentrations of Aromatic Hydrocarbons in Filtered Water from Nine Sampling Sites in Puget Sound, $\bar{x} \pm SE$, Parts Per Trillion (pptr) Dry Weight Sediment

Compound	Seattle P-54 ¹	Seattle HI	Seattle WW	Bremerton SI	Tacoma PR	Tacoma HW	Tacoma BW	Olympia BI	Port Madison
Naphthalene	108 \pm 18	30 \pm 1	38 \pm 1	20 \pm 2	20 \pm 27	74 \pm 8	58 \pm 18	21 \pm 0	18 \pm 8
2-MN	13 \pm 6	4 \pm 4	8 \pm 9	14 \pm 1	13 \pm 15	16 \pm 11	27 \pm 5	7 \pm 7	20 \pm 1
1-MN	15 \pm 5	3 \pm 2	10 \pm 1	7 \pm 0	6 \pm 9	11 \pm 8	17 \pm 6	7 \pm 0	9 \pm 1
2,6-DMN	3 \pm 4	3 \pm 3	2 \pm 1	<1	4 \pm 1	7 \pm 2	2 \pm 2	<1	1 \pm 1
1,3-DMN	2 \pm 2	3 \pm 1	3 \pm 0	2 \pm 0	3 \pm 1	5 \pm 1	4 \pm 1	2 \pm 1	3 \pm 1
2,3-DMN	2 \pm 3	<1	<1	<1	1 \pm 1	5 \pm 0	3 \pm 2	<1	<1
2,3,6-TMN	6 \pm 4	5 \pm 3	7 \pm 1	12 \pm 1	4 \pm 4	7 \pm 2	4 \pm 2	5 \pm 3	7 \pm 0
Fluorene	30 \pm 8	<1	<1	<1	3 \pm 2	<1	<1	<1	<1
Phenanthrene	24 \pm 29	13 \pm 1	14 \pm 2	2 \pm 0	12 \pm 2	18 \pm 12	5 \pm 2	5 \pm 1	1 \pm 0
Anthracene	<1	<1	<1	<1	<1	<1	<1	<1	<1
1-MP	59 \pm 28	59 \pm 17	41 \pm 0	50 \pm 13	30 \pm 39	22 \pm 18	50 \pm 24	52 \pm 23	39 \pm 4
2-MP	69 \pm 59	34 \pm 31	57 \pm 19	59 \pm 74	274 \pm 108	25 \pm 23	40 \pm 54	102 \pm 2	29 \pm 13
Fluoranthene	<1	<1	<1	<1	<1	<1	<1	25 \pm 35	<1
Pyrene	11 \pm 1	12 \pm 1	10 \pm 1	9 \pm 11	4 \pm 3	5 \pm 1	9 \pm 2	3 \pm 2	21 \pm 8
1-Me Pyrene	<1	<1	<1	<1	<1	<1	<1	<1	<1
B(a)A	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chrysene	<1	<1	<1	<1	<1	<1	<1	<1	<1
TOTAL	311 \pm 33	165 \pm 18	190 \pm 76	173 \pm 74	369 \pm 423	179 \pm 8	239 \pm 37	203 \pm 13	93 \pm 118

¹P-54 = Pier 54, HI = Harbor Island, WW = West Waterway, SI = Sinclair Inlet, PR = Puyallup River, HW = Hylebos Waterway, BW = Blair Waterway, BI = Budd Inlet

Table 12. Seasonal Variation in the Concentrations of Aromatic Hydrocarbons from Filtered Water from Hylebos Waterway (Tacoma) and Blair Waterway (Tacoma), $\bar{x} \pm SE$, Parts Per Trillion (pptr)

Compound	Hylebos Waterway			Blair Waterway		
	Jul 1979	Sep 1979	Nov 1979 ²	Jul 1979	Sep 1979	Nov 1979
Naphthalene	74 \pm 8	<3	47	58 \pm 18	<2	26 \pm 6
2-MN	16 \pm 11	<3	20	27 \pm 5	<2	7 \pm 5
1-MN	11 \pm 8	<3	<8	17 \pm 6	<2	3 \pm 4
2,6-DMN	7 \pm 2	<4	<2	2 \pm 2	<3	<2
1,3-DMN	5 \pm 1	<4	<2	4 \pm 1	<3	<2
2,3-DMN	5 \pm 0	<3	<2	3 \pm 2	<3	<2
2,3,6-TMN	7 \pm 2	<4	<2	4 \pm 2	<3	<2
Fluorene	<1	<4	<2	<1	<3	<2
Phenanthrene	18 \pm 12	<4	<2	5 \pm 2	<3	<2
Anthracene	<1	<4	<2	<1	<3	<2
1-MP ¹	22 \pm 18	<4	<2	50 \pm 24	<3	<2
2-MP ¹	25 \pm 23	<4	<3	40 \pm 54	<3	<3
Fluoranthene	<1	<4	<3	<1	<3	<2
Pyrene		<4	<3	9 \pm 2	<3	<3
1-Me Pyrene	<1	<4	<4	<1	<3	<3
B(a)A	<1	<4	<3	<1	<3	<3
Chrysene	<1	<4	<3	<1	<3	<3
TOTAL	389 \pm 372	--	75	239 \pm 37	--	35 \pm 16

¹High concentrations for these compounds at the July 1979 sampling of Hylebos Waterway and Blair Waterway are due to septum bleed.

²Only one sample analyzed.

Table 13. Concentrations of Saturate Hydrocarbons Associated with Suspended Matter from Nine Sampling Sites in Puget Sound, $\bar{x} \pm \text{SE}$, Parts Per Million (ppm) Dry Weight Sediment

Compound	Seattle P-54 ¹	Seattle HI	Seattle WW	Bremerton SI	Tacoma PR	Tacoma HW	Tacoma BW	Olympia BI	Port Madison
C ₁₃	0.2 \pm 0.0	0.2 \pm 0.0	0.8 \pm 0.2	1.7 \pm 0.8	1.5 \pm 0.8	1.8 \pm 1.2	0.7 \pm 0.2	0.6 \pm 0.4	0.4 \pm 0.2
C ₁₄	0.3 \pm 0.0	0.5 \pm 0.0	0.7 \pm 0.1	2.3 \pm 1.0	1.9 \pm 0.6	3.0 \pm 1.9	1.6 \pm 0.5	0.4 \pm 0.1	0.5 \pm 0.5
C ₁₅	0.7 \pm 0.1	0.9 \pm 0.0	0.7 \pm 0.1	3.2 \pm 1.4	1.9 \pm 1.0	4.2 \pm 2.5	1.7 \pm 0.6	2.1 \pm 1.2	2.4 \pm 1.3
C ₁₆	0.6 \pm 0.1	1.0 \pm 0.0	0.7 \pm 0.1	2.9 \pm 1.3	1.8 \pm 1.0	4.6 \pm 2.6	1.3 \pm 0.3	0.3 \pm 0.1	1.7 \pm 1.1
C ₁₇	1.2 \pm 0.0	1.8 \pm 0.1	1.5 \pm 0.2	3.8 \pm 1.3	3.1 \pm 1.6	5.7 \pm 2.9	3.0 \pm 1.1	13.2 \pm 7.5	4.6 \pm 1.9
Pristane	3.1 \pm 0.2	2.8 \pm 0.0	3.2 \pm 0.7	5.1 \pm 1.3	1.9 \pm 0.8	4.0 \pm 2.1	2.4 \pm 0.9	2.2 \pm 1.4	50.6 \pm 27.4
C ₁₈	0.7 \pm 0.1	1.3 \pm 0.1	1.0 \pm 0.2	2.6 \pm 1.0	2.3 \pm 1.2	4.7 \pm 2.2	1.6 \pm 0.5	0.8 \pm 0.2	0.4 \pm 0.1
Phytane	0.5 \pm 0.0	1.0 \pm 0.1	0.9 \pm 0.1	1.2 \pm 0.4	1.4 \pm 0.6	2.5 \pm 1.2	1.3 \pm 0.4	0.2 \pm 0.0	0.4 \pm 0.1
C ₁₉	1.0 \pm 0.1	1.6 \pm 0.2	1.5 \pm 0.5	3.6 \pm 0.7	2.7 \pm 1.3	5.0 \pm 2.2	3.1 \pm 1.8	9.5 \pm 2.1	0.6 \pm 0.0
C ₂₀	0.7 \pm 0.1	1.1 \pm 0.1	1.2 \pm 0.1	2.6 \pm 0.3	1.8 \pm 0.8	3.5 \pm 1.5	2.1 \pm 1.3	27.6 \pm 21.9	0.8 \pm 0.2
C ₂₁	0.7 \pm 0.1	1.1 \pm 0.3	1.1 \pm 0.7	1.9 \pm 0.4	2.2 \pm 0.9	3.2 \pm 1.4	1.6 \pm 0.4	4.4 \pm 2.2	0.5 \pm 0.0
C ₂₂	0.6 \pm 0.0	1.2 \pm 0.8	0.7 \pm 0.1	1.3 \pm 0.7	1.6 \pm 0.7	2.6 \pm 1.0	2.7 \pm 2.6	1.0 \pm 0.7	0.2 \pm 0.1
C ₂₃	0.5 \pm 0.2	0.9 \pm 0.6	1.4 \pm 0.8	0.5 \pm 0.4	1.8 \pm 0.8	1.2 \pm 0.2	2.2 \pm 2.4	0.6 \pm 0.1	0.6 \pm 0.8
C ₂₄	0.4 \pm 0.0	0.3 \pm 0.0	0.5 \pm 0.0	0.4 \pm 0.0	1.7 \pm 0.8	2.3 \pm 0.9	1.3 \pm 0.6	4.8 \pm 2.2	0.1 \pm 0.2
TOTAL	11.3 \pm 0.7	15.9 \pm 2.2	15.7 \pm 1.9	32.8 \pm 8.7	28.5 \pm 13.9	48.2 \pm 24.0	26.4 \pm 13.7	67.6 \pm 35.9	63.3 \pm 31.5

¹p-54 = Pier 54, HI = Harbor Island, WW = West Waterway, SI = Sinclair Inlet, PR = Puyallup River, HW = Hylebos Waterway, BW = Blair Waterway, BI = Budd Inlet

Table 14. Seasonal Variation in the Concentrations of Saturate Hydrocarbons Associated with Suspended Matter from Hylebos Waterway (Tacoma) and Blair Waterway (Tacoma), $\bar{x} \pm \text{SE}$, Parts Per Million (ppm) Dry Weight Sediment

Compound	Hybelos Waterway			Blair Waterway		
	Jul 1979	Sep 1979	Nov 1979	Jul 1979	Sep 1979	Nov 1979
C ₁₃	1.8 \pm 1.2	0.6 \pm 0.2	1.8 \pm 1.0	0.7 \pm 0.2	0.1 \pm 0.1	1.4 \pm 0.3
C ₁₄	3.0 \pm 1.9	1.6 \pm 0.2	2.8 \pm 1.5	1.6 \pm 0.5	0.7 \pm 0.0	2.1 \pm 0.5
C ₁₅	4.2 \pm 2.5	1.6 \pm 0.1	3.1 \pm 1.4	1.7 \pm 0.6	0.6 \pm 0.0	2.2 \pm 0.3
C ₁₆	4.6 \pm 2.6	1.7 \pm 0.1	2.2 \pm 1.1	1.3 \pm 0.3	0.7 \pm 0.1	1.8 \pm 0.2
C ₁₇	5.7 \pm 2.9	2.5 \pm 0.3	2.5 \pm 1.1	3.0 \pm 1.1	1.3 \pm 0.4	2.4 \pm 0.2
Pristane	4.0 \pm 2.1	2.5 \pm 0.2	2.5 \pm 0.9	2.4 \pm 0.9	3.3 \pm 0.5	3.4 \pm 0.4
C ₁₈	4.7 \pm 2.2	2.2 \pm 0.4	2.3 \pm 0.8	1.6 \pm 0.5	0.8 \pm 0.1	1.9 \pm 0.1
Phytane	2.5 \pm 1.2	1.4 \pm 0.0	2.2 \pm 1.3	1.3 \pm 0.4	1.2 \pm 0.2	1.5 \pm 0.2
C ₁₉	5.0 \pm 2.2	1.6 \pm 0.4	2.1 \pm 0.3	3.1 \pm 1.8	1.2 \pm 0.0	2.4 \pm 0.5
C ₂₀	3.5 \pm 1.5	1.3 \pm 0.1	1.9 \pm 0.5	2.1 \pm 1.3	0.6 \pm 0.1	1.5 \pm 0.3
C ₂₁	3.2 \pm 1.4	1.5 \pm 0.1	2.3 \pm 1.2	1.6 \pm 0.4	0.7 \pm 0.2	1.4 \pm 0.2
C ₂₂	2.6 \pm 1.0	1.0 \pm 0.2	3.0 \pm 3.0	2.7 \pm 2.6	1.0 \pm 0.7	1.5 \pm 0.0
C ₂₃	1.2 \pm 0.2	0.7 \pm 0.0	4.9 \pm 6.0	2.2 \pm 2.4	<0.1	0.9 \pm 0.0
C ₂₄	2.3 \pm 0.9	0.8 \pm 0.0	1.0 \pm 0.5	1.3 \pm 0.6	0.5 \pm 0.4	0.9 \pm 0.1
TOTAL	48.2 \pm 24.0	20.9 \pm 0.6	34.6 \pm 17.8	26.4 \pm 13.7	12.6 \pm 0.1	25.3 \pm 3.5

Table 15. Concentrations of Aromatic Hydrocarbons Associated with Suspended Matter from Nine Sampling Sites in Puget Sound, $\bar{x} \pm \text{SE}$, Parts Per Million (ppm) Dry Weight Sediment

Compound	Seattle P-54 ¹	Seattle HI	Seattle WW	Bremerton SI	Tacoma PR	Tacoma HW	Tacoma BW	Olympia BI	Port Madison
Naphthalene	0.02 \pm 0.01	0.02 \pm 0.01	0.03 \pm 0.01	0.03 \pm 0.00	0.42 \pm 0.14	0.05 \pm 0.03	0.23 \pm 0.08	0.02 \pm 0.00	0.02 \pm 0.01
2-MN ²	0.02 \pm 0.00	0.02 \pm 0.01	0.02 \pm 0.00	0.02 \pm 0.01	0.03 \pm 0.00	0.02 \pm 0.01	0.01 \pm 0.01	0.05 \pm 0.03	0.01 \pm 0.00
1-MN	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.01	0.03 \pm 0.02	0.02 \pm 0.00	0.02 \pm 0.02	0.01 \pm 0.01	0.19 \pm 0.14	0.17 \pm 0.21
2,6-DMN	0.02 \pm 0.01	0.01 \pm 0.01	0.01 \pm 0.00	0.07 \pm 0.04	<0.01	0.10 \pm 0.11	0.05 \pm 0.06	0.03 \pm 0.03	0.10 \pm 0.02
1,3-DMN	<0.01	0.01 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.01	0.01 \pm 0.01	0.14 \pm 0.11	<0.01	0.02 \pm 0.01	0.02 \pm 0.00
2,3-DMN	0.01 \pm 0.01	0.01 \pm 0.00	<0.01	0.02 \pm 0.00	<0.01	0.02 \pm 0.03	0.02 \pm 0.02	0.01 \pm 0.01	0.01 \pm 0.01
2,3,6-TMN	0.02 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.00	0.13 \pm 0.07	0.07 \pm 0.03	0.73 \pm 0.64	0.03 \pm 0.05	0.04 \pm 0.01	0.06 \pm 0.09
Fluorene	0.05 \pm 0.01	0.04 \pm 0.06	<0.01	0.07 \pm 0.10	0.04 \pm 0.06	<0.01	<0.01	0.05 \pm 0.01	0.01 \pm 0.02
Phenanthrene	0.27 \pm 0.03	0.14 \pm 0.09	0.22 \pm 0.04	0.10 \pm 0.04	0.27 \pm 0.06	0.62 \pm 0.26	0.28 \pm 0.13	0.12 \pm 0.13	0.08 \pm 0.02
Anthracene	0.18 \pm 0.02	<0.01	0.08 \pm 0.02	<0.01	<0.01	0.13 \pm 0.18	<0.01	0.09 \pm 0.04	0.41 \pm 0.44
1-MP	0.01 \pm 0.02	0.01 \pm 0.01	<0.01	0.05 \pm 0.02	0.06 \pm 0.02	0.19 \pm 0.26	0.22 \pm 0.04	0.01 \pm 0.01	0.05 \pm 0.06
2-MP	0.04 \pm 0.02	0.10 \pm 0.08	0.08 \pm 0.03	0.10 \pm 0.00	0.22 \pm 0.16	0.48 \pm 0.68	0.45 \pm 0.64	0.10 \pm 0.14	0.34 \pm 0.24
Fluoranthene	0.37 \pm 0.05	0.25 \pm 0.09	0.36 \pm 0.11	0.54 \pm 0.33	2.34 \pm 0.44	0.83 \pm 0.08	3.45 \pm 1.62	0.08 \pm 0.02	0.15 \pm 0.00
Pyrene	0.49 \pm 0.17	0.21 \pm 0.20	0.58 \pm 0.21	0.97 \pm 0.49	3.94 \pm 0.94	0.51 \pm 0.71	2.94 \pm 1.29	0.21 \pm 0.09	1.05 \pm 0.40
1-Me-Pyrene	<0.01	<0.01	<0.01	<0.02	<0.01	0.11 \pm 0.15	<0.02	<0.01	<0.01
B(a)A	0.08 \pm 0.00	0.03 \pm 0.01	0.07 \pm 0.02	<0.02	<0.01	0.01 \pm 0.01	<0.01	<0.01	<0.01
Chrysene	0.13 \pm 0.00	0.05 \pm 0.00	0.12 \pm 0.04	<0.01	<0.01	0.04 \pm 0.06	<0.01	<0.01	<0.01
B(a)P	0.02 \pm 0.03	<0.01	<0.01	<0.01	0.12 \pm 0.17	0.04 \pm 0.05	<0.01	<0.01	<0.01
Perylene	0.03 \pm 0.04	<0.01	<0.01	<0.01	0.18 \pm 0.26	0.06 \pm 0.09	<0.01	<0.01	<0.01
TOTAL	1.76 \pm 0.07	0.90 \pm 0.15	1.6 \pm 0.50	2.1 \pm 0.73	7.71 \pm 0.93	4.08 \pm 1.02	7.67 \pm 1.37	1.01 \pm 0.62	2.48 \pm 0.05

¹P-54 = Pier 54, HI = Harbor Island, WW = West Waterway, SI = Sinclair Inlet, PR = Puyallup River, HW = Hylebos Waterway, BW = Blair Waterway, BI = Budd Inlet

²MN = methylnaphthalene, DMN = dimethylnaphthalene, TMN = trimethylnaphthalene, MP = methylphenanthrene, 1-Me-Pyrene = 1-methylpyrene, B(a)A = Benz(a)anthracene, B(a)P = Benz(a)pyrene

Table 16. Seasonal Variation in the Concentrations of Aromatic Hydrocarbons Associated with Suspended Matter from Hylebos Waterway (Tacoma) and Blair Waterway (Tacoma), $\bar{x} \pm SE$, Parts Per Million (ppm) Dry Weight Sediment

Compound	Hybelos Waterway			Blair Waterway		
	Jul 1979	Sep 1979	Nov 1979	Jul 1979	Sep 1979	Nov 1979
Naphthalene	0.05 \pm 0.03	<0.03	0.29 \pm 0.09	0.23 \pm 0.08	0.16 \pm 0.08	0.26 \pm 0.03
2-MN	0.02 \pm 0.01	<0.03	0.07 \pm 0.01	0.01 \pm 0.01	<0.01	<0.03
1-MN	0.02 \pm 0.02	<0.03	0.07 \pm 0.05	0.01 \pm 0.01	<0.01	<0.03
2,6-DMN	0.10 \pm 0.11	<0.03	0.01 \pm 0.02	0.05 \pm 0.06	<0.01	<0.03
1,3-DMN	0.14 \pm 0.11	<0.03	0.02 \pm 0.03	<0.01	<0.01	<0.03
2,3-DMN	0.02 \pm 0.03	<0.02	<0.02	0.02 \pm 0.02	<0.01	<0.03
2,3,6-TMN	0.73 \pm 0.64	<0.04	0.65 \pm 0.77	0.03 \pm 0.05	<0.02	0.03 \pm 0.04
Fluorene	<0.01	<0.04	<0.02	<0.01	<0.02	0.03 \pm 0.05
Phenanthrene	0.62 \pm 0.26	0.17 \pm 0.04	0.65 \pm 0.19	0.28 \pm 0.13	<0.01	0.55 \pm 0.04
Anthracene	0.13 \pm 0.18	0.22 \pm 0.31	0.21 \pm 0.14	<0.01	<0.01	0.27 \pm 0.05
1-MP	0.19 \pm 0.26	<0.04	0.40 \pm 0.47	0.22 \pm 0.04	<0.02	0.04 \pm 0.05
2-MP	0.48 \pm 0.68	<0.04	0.11 \pm 0.01	0.45 \pm 0.64	1.79 \pm 0.61	0.42 \pm 0.08
Fluoranthene	0.83 \pm 0.08	1.31 \pm 1.16	1.56 \pm 0.82	3.45 \pm 1.62	3.04 \pm 1.84	1.21 \pm 0.15
Pyrene	0.51 \pm 0.71	1.17 \pm 0.91	1.67 \pm 0.82	2.94 \pm 1.29	2.38 \pm 1.45	1.32 \pm 0.12
1-Me-Pyrene	0.11 \pm 0.15	<0.04	2.48 \pm 3.06	<0.02	<0.02	<0.05
B(a)A	0.01 \pm 0.01	<0.03	0.43 \pm 0.16	<0.01	0.10 \pm 0.14	0.34 \pm 0.07
Chrysene	0.04 \pm 0.06	<0.04	1.20 \pm 0.38	<0.01	0.26 \pm 0.36	1.2 \pm 0.48
B(a)P	0.04 \pm 0.05	<0.05	0.15 \pm 0.21	<0.01	<0.02	2.35 \pm 3.32
Perylene	0.06 \pm 0.09	<0.06	1.33 \pm 0.37	<0.01	<0.01	3.58 \pm 1.12
TOTAL	4.08 \pm 1.02	2.88 \pm 1.53	11.35 \pm 6.18	7.67 \pm 1.37	7.07 \pm 3.26	11.58 \pm 4.19

6. ACKNOWLEDGMENTS

Name brands found throughout the text and Appendixes are used to assure understanding of the methods and materials employed during the study. Their use does not imply endorsement by Battelle Memorial Institute.

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APPENDIX A
SAMPLING METHODS

APPENDIX A

SAMPLING METHODS

Sampling Preparation at Nine Stations

Sampling was conducted from a Battelle-Northwest research vessel anchored at the sampling stations. The locations of the nine sites are listed in Section II and shown on charts in Appendix A. The depth below the surface from which the water was collected was based on the turbidity of the water, as determined by a 1-meter path length transmissometer. The depth of maximum turbidity was sampled and was usually in the 1-3 m depth range (Table 1). Each site was occupied for three to four hours to allow time to collect integrated samples or several individual samples as in the case of salinity and chlorophyll. Sampling occurred primarily during ebbing tides.

Sampling for Chlorophyll, Particulate Organic Carbon, Dissolved Organic Carbon, and Salinity

At each site, duplicate samples were collected from the Niskin bottles for chlorophyll, particulate organic carbon, dissolved oxygen, and salinity. Samples were collected for chlorophyll analysis by filtering a known volume of sea water through a 47 millimeter diameter membrane (0.4 micron pore size) filter using the procedure described in Strickland and Parsons (1972). Particulate organic carbon samples were collected by filtration of several hundred milliliters of sea water through a precombusted glass fiber filter. The filter was stored frozen. Ten milliliters of the filtrate from each of the particulate organic carbon collections was stored under refrigeration for dissolved organic carbon analysis.

Sampling Suspended Matter for Metals

Suspended matter samples (10 to 100 mg dry wt) were collected in duplicate by pressure filtration of 5-20 liters of sea water through a 0.4 micron membrane filter. Water was collected for filtration by repeated grab sampling with a teflon-coated water GoFlo Niskin bottle. After pressure filtration by N_2 gas, the sample was rinsed with a small volume of high purity distilled water to remove soluble salts in order to determine an accurate weight of the suspended matter. The samples were refrigerated during transport and storage.

Sampling of Water for Purgable Organic Compounds

Glass bottles (125 milliliters) used for collection of "purge and trap" samples were cleaned with soap and water, rinsed rigorously with distilled water and dried in an oven at 120°C for several hours. The bottles were cooled and capped with a Hycar septum to prevent reintroduction of contamination prior to sample collection. Samples for "purge and trap" analysis were collected by removing the septum cap, completely filling the bottle with Puget

Sound water and recapping with another Hycar septum. Three to four samples were collected at each sample site. Samples were kept at wet ice temperature during sampling cruises, transport to the Battelle Marine Research Laboratory at Sequim, and transport to the Battelle Laboratories in Richland, Washington. Samples were stored in the refrigerator at 4°C until analyzed.

Sampling of Filtered Water for Saturated, Aromatic and Halogenated Hydrocarbons

Preparation of Resin

XAD-2 Resin obtained from Supelco, Inc. or Rohm and Haas was cleaned of impurities by three sequential soxhlet extractions with methanol, acetonitrile and anhydrous ether respectively. Each extraction lasted 24 hours. After the ether extraction, the resin was rinsed thoroughly with methanol and stored in a glass stoppered jar under methanol.

Preparation of Columns

Cleaned (sonicated in soap and water, rinsed with distilled water and dried with acetone) stainless steel columns (5/8" O.D. x 9" in length) and fitted with swagelok stainless steel 5/8 to 1/4 inch reducing unions were connected to vacuum (aspirator). After addition of a plug of silanized glass wool to the bottom of the column, XAD-2 resin which had been slurried with methanol was added until just sufficient space remains to add a small plug of glass wool at the top. Following addition of the resin, each end of the column was tightly sealed off with 1/4 inch stainless steel plugs. The columns were stored in a refrigerator until they were used.

Sampling at Station

During the collection of suspended particulates, the glass filtered water was sampled for soluble hydrocarbons and halogenated organics by pumping 20 liters of the water over XAD-2 resin contained in small stainless steel columns. The columns were stored refrigerated until analyzed.

Sampling of Suspended Matter for Hydrocarbon and Halogenated Organics Analysis

Suspended particulates (10 to 100 g, wet wt) were collected in triplicate by filtration of approximately 2000 liters of water through a glass-fiber filter with an effective pore size of 0.5 microns. The filters were precleaned by combustion at 450°C for two hours. The glass filters retained 98% ± 0.5% of the particulate material compared to 0.4 micron membrane filters. Sampling apparatus consisted of a steel pump, a PVC hose and a PVC Battelle large volume filter holder (Silker et al., 1971). The filter holder held eight filters in parallel, each 30 cm in diameter. The sampling apparatus was precleaned with detergent. The system blank due to filters, filter holder, pump and hose was insignificant. The particulate material was stored frozen in wide-mouth glass jars containing metal-lined caps.

APPENDIX B
ANALYTICAL METHODS

APPENDIX B

ANALYTICAL METHODS

Total Suspended Matter

The concentration of total suspended matter (micrograms per liter) was determined by weighing after oven-drying at 60°C to constant weight.

Particulate Organic and Dissolved Organic Carbon

The concentrations of particulate organic carbon and dissolved organic carbon were determined by wet oxidation of carbon to CO₂ in sealed ampules after inorganic carbon was removed. The CO₂ produced was quantified by IR light absorbtion using a Oceanography International carbon analyzer.

Chlorophyll A

The concentration of chlorophyll a was determined by measuring the extinction of light in the acetone extraction solution, according to Strickland and Parsons (1972).

Salinity, Temperature, and Dissolved Oxygen

Salinity was determined using a Hytech salinometer standardized with standard sea water. The temperature and dissolved oxygen was determined immediately after collection of the water by Niskin bottle using an oxygen electrode and temperature probe. The dissolved oxygen electrode was calibrated in air equilibrated fresh water and by the Winkler titration (Strickland and Parsons, 1972).

Elemental Analysis of Suspended Matter

Suspended matter samples and the intercomparison sediment samples were analyzed by Instrumental Neutron Activation Analysis (INAA) and energy dispersive X-ray fluorescence (XRF). NBS environmental standards and U.S. Geological Survey standard rocks were used to calibrate the instruments. The procedure for our INAA is described by Ondov et al. (1975). The XRF analytical procedure used in our laboratory and the results for 24 elements in standard reference materials are described by Nielson (1977).

The analytical uncertainty for both techniques as determined by replicate analysis of a single sample, is usually not more than +5% for one standard deviation. The uncertainty in the data due to variability among duplicate samples from a single station is approximately $\pm 20\%$ for one standard deviation.

Purge and Trap Analysis

The procedure used for this analysis is very similar to that discussed by Bellar and Lichtenberg (1974). A sample of water containing the volatile organics is sparged with nitrogen gas and then passed through a stainless steel column packed with porous polymer beads (in this case, Tenax). Volatile organics, which are adsorbed on the polymer, are then introduced into the gas chromatograph (GC) or gas chromatograph/mass spectrometer (GC/MS) by heating the Tenax trap at about 200°C in a stream of helium. This process desorbs the organics from the trap and adsorbs them on to the front of the chromatographic column held at 0°C. After the volatiles have been introduced onto the column, they are separated by conventional temperature-programmed gas chromatography.^a

An important part of the procedure is the prevention of water sample exposure to an air interface prior to sparging, since the volatiles are rapidly lost to air. To avoid this loss, two hypodermic needles were inserted through the sample bottle septum, one of which was attached to a 100 ml glass syringe fitted with a stopcock valve. About 80 ml of water sample was then carefully drawn into the syringe and the valve closed. Thirty-five milliliters of sample was expressed from the syringe into the sparging apparatus through a small-bore teflon tube, filling the apparatus from the bottom up. The remainder of the sample was stored in the syringe as a contingency sample. Just prior to sparging, one microliter of an ethanolic solution of internal standard mixture containing 0.8 mg each of bromochloromethane (Int. Std. #1, Fig. B-1), 1,4-dichlorobutane (Int. Std. #2, Fig. B-2) and 1-chloro-2-bromopropane (Int. Std. #3)^b was added. Nitrogen purge of the sample was at 30 ml/min for 20 minutes.

Separation of volatile components was accomplished on a 2 mm ID glass 6-ft column packed with 0.2% carbowax 1500 on carbopack, using 20 ml/min helium carrier. After an initial hold at 0°C for sample introduction (5.5 min), the chromatographic oven was brought to 45°C in 1.5 min and then programmed at 8°C to 160°C. Instrumentation was a Hewlett-Packard Model 5985GC/MS System, including a Model 5840A Gas Chromatograph. Mass spectra were obtained by scanning in the electron impact mode from mass 45 to 320 at 180 amu/sec at an electron multiplier voltage of 2,200.

Total ionization chromatograms of two sets of analytical standards containing 23 of the components designated as EPA priority pollutants (Environmental Protection Agency, 1977) are presented in Fig. B-1 and B-2. All samples analyzed by the "purge and trap" technique were examined for spectra indicative of these components. Levels at which components could be quantitated are

^aThe porous polymer traps, sparging apparatus, GC adapters, and column heater are available from Envirotech Equipment Company as part of a Trace Organic Kit.

^bThe internal standard mixture is a dilution of a mixture supplied by Supelco, Inc. Int. Std. #3 did not give spectra characteristic of the bromo compound; the spectra was consistent with 2-chloro-2-butene.

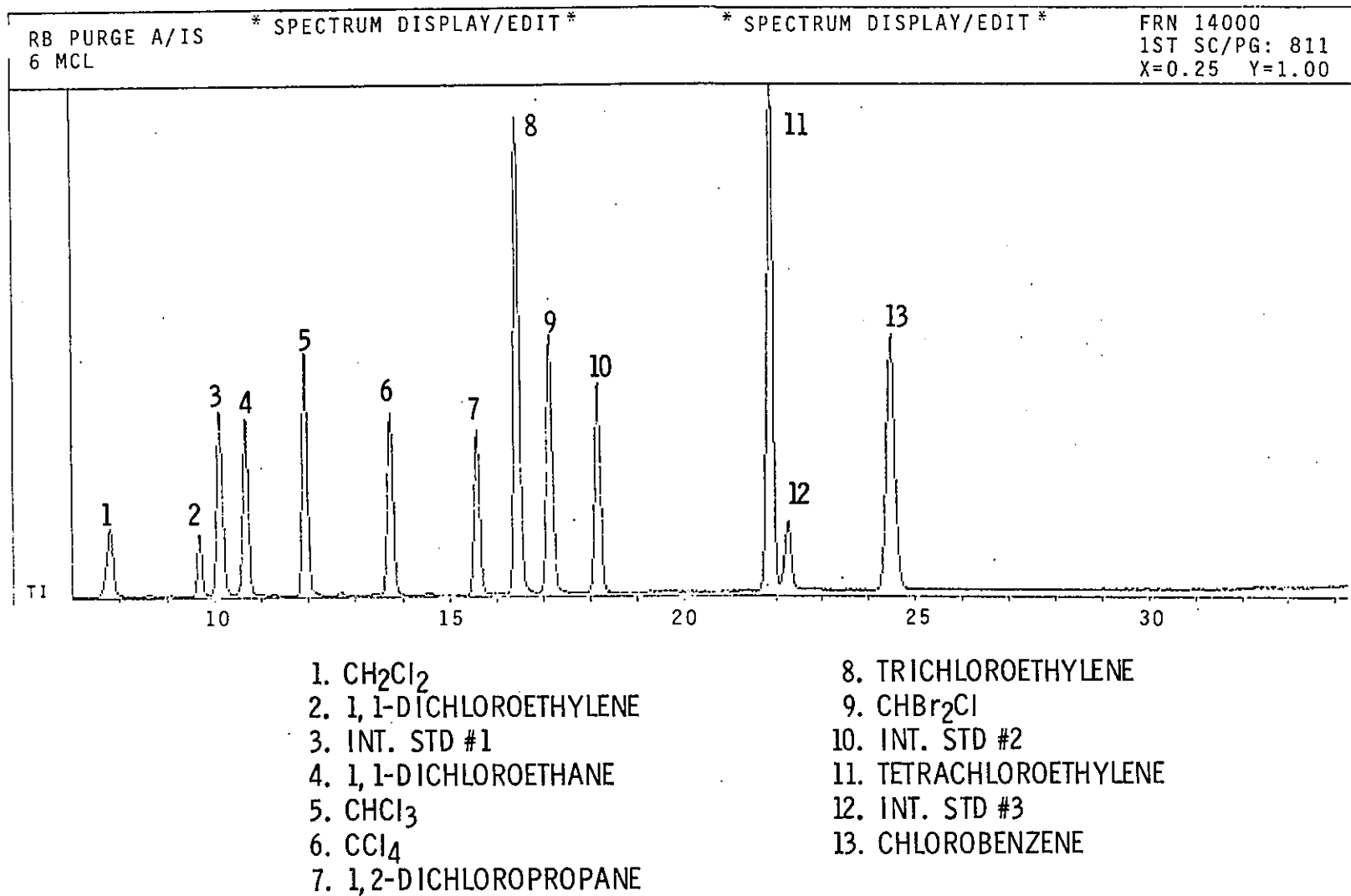


Figure B-1. Total ionization chromatogram of purge and trap standards mixture "A".
Component concentrations are about 34 µg/l in water.

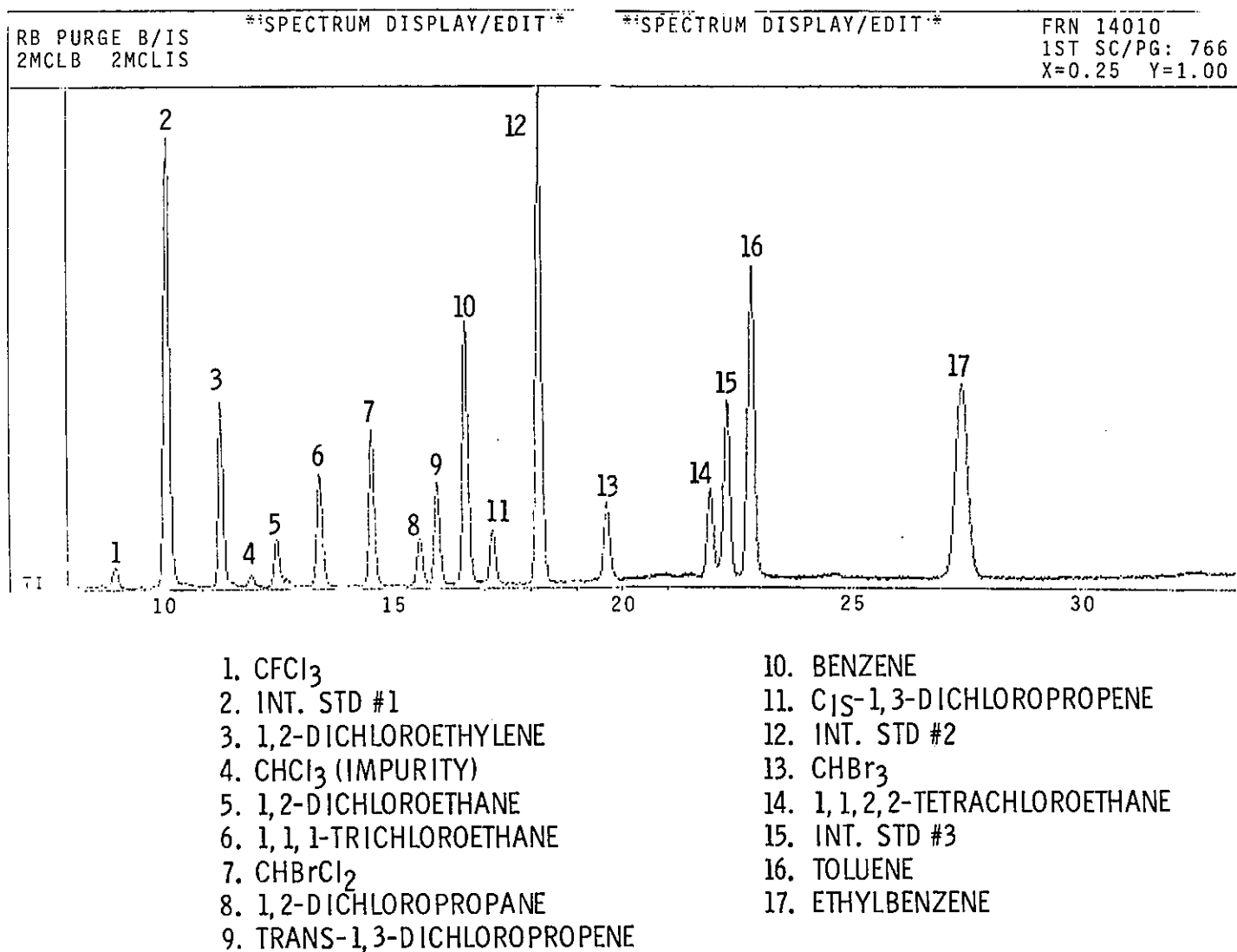


Figure B-2. Total ionization chromatograms of purge and trap standards mixture "B".
Component concentrations are about 11 µg/l in water.

estimated to be 0.5 milligrams per liter. Detection levels are lower than this (>0.1 mg/ml) when reconstructed single ion chromatograms were examined.

Three criteria were used for identification of purgable organic compounds:

- Relative retention time of unknown compound must agree with that of the standard compound.
- Single ion reconstructed traces of major ions of unknown compound are present.
- Isotope ratios of major ions must agree closely with theoretical ratios in background subtracted spectra.

If all three criteria are met, a positive identification is assigned. If criteria 1 and 3 are met, a positive identification is assigned; however, concentrations may not be sufficient for quantitation. If criteria 1 and 2 are met, a tentative identification is assigned (designated by question marks in Table 6). Fig. B-3A and B-3B show single ion reconstructed mass chromatograms and mass spectrum for tentative identification of tetrachloroethylene in Puget Sound water whereas Fig. B-3C and B-3D show the same information for a positive identification of tetrachloroethylene in Puget Sound water.

Analysis of Saturated, Aromatic and Halogenated Hydrocarbons in Water by Adsorption on XAD-2 Resin

Hydrocarbons sorbed to XAD-2 resin contained in stainless columns were eluted with 100 ml of ethyl ether. Water underneath the ether extracts was removed with a Pasteur pipette and the ether was dried overnight in the presence of anhydrous sodium sulfate. The dried ether extracts were concentrated under a stream of dry nitrogen, transferred to solution vials and concentrated to 1 milliliter volumes. The solvent was exchanged from ether to hexane by the addition of 1 ml of hexane and reconcentration to 1 ml under a stream of nitrogen. The concentrated extracts were passed through a glass column containing 15 grams of activated silica gel (Davidson 100-200 mesh, Supelco, Inc.) such that saturated (40 ml hexane) and aromatic (86 ml of 20% methylene chloride in hexane) hydrocarbon fractions were collected. Individual samples were concentrated following addition of 1 ml of internal standard to 0.3 to 1 ml under a stream of nitrogen and analyzed by capillary gas chromatography or capillary gas chromatography-mass spectrometry.

Quantitation of saturated and aromatic hydrocarbons were made, where possible, according to calibrations made with known standards on a Hewlett Packard 5840-A gas chromatograph containing a 30 meter SP-2100 glass capillary column (J&W Scientific) and flame ionization detector using 2,6,10-trimethyl-dodecane and hexamethylbenzene as internal standards for the saturated and aromatic fractions respectively. Chromatographic runs were initiated at 70°C with a 4 minute hold followed by a temperature program at 4°/min to 250°C with a hold at 250°C for 15 minutes. Filter blanks and system blanks were analyzed

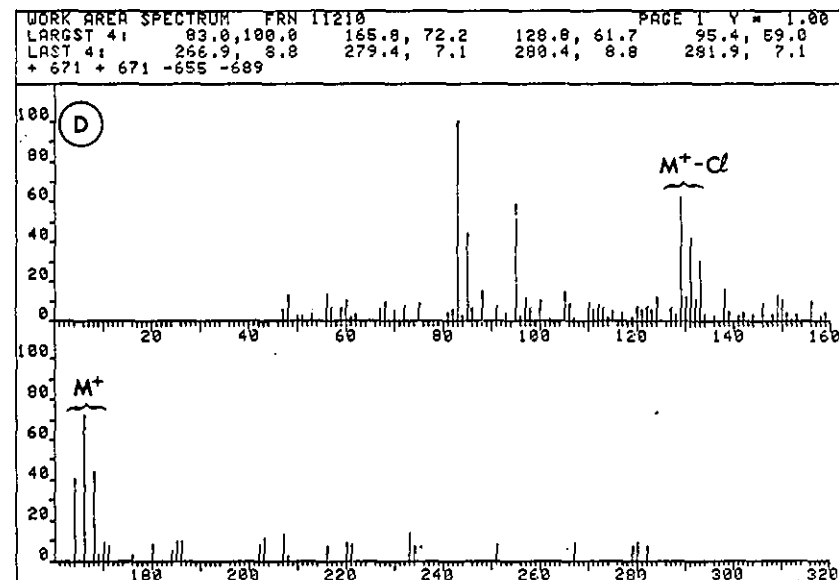
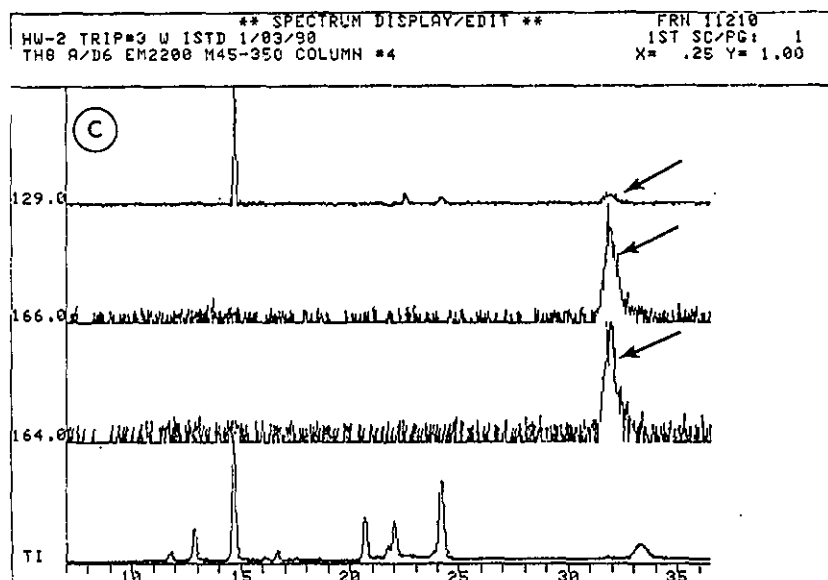
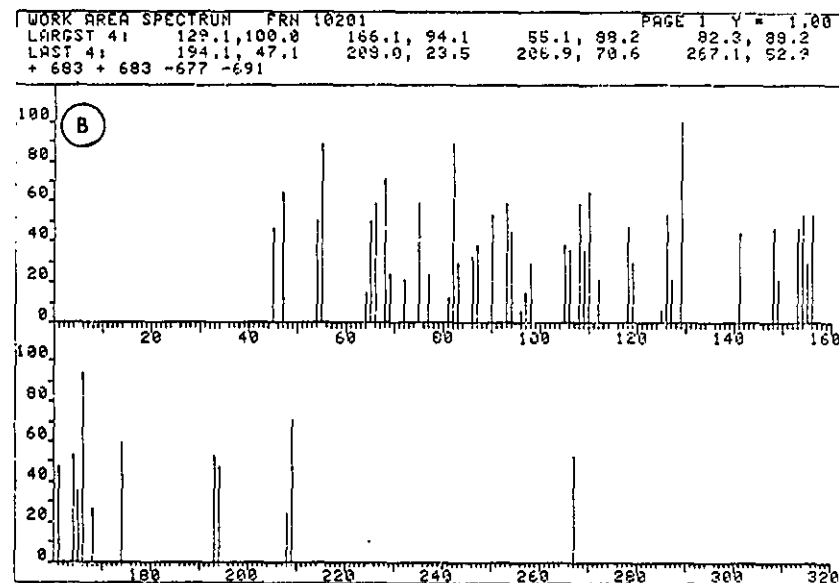
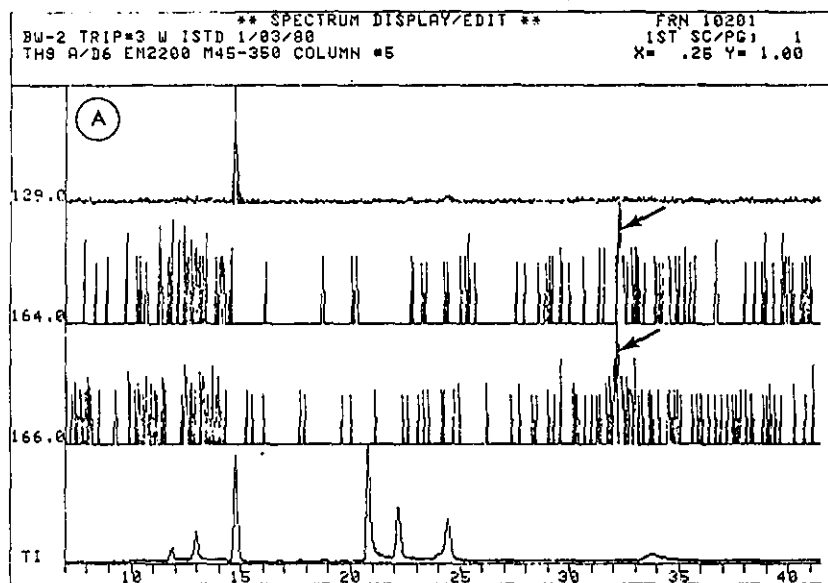


Figure B-3. Total ion mass chromatograms and mass spectra of tentatively identified (A+B) and positively identified (C+D) of tetrachloroethylene in purgable water sample from Puget Sound.

regularly for compounds that could interfere with quantitation and all quantitated compounds were corrected for recovery based on the recovery of analytical standards from the sample preparation scheme.

One half of the aromatic fraction was used to qualitatively analyze for the presence of halogenated organic compounds using the same gas chromatographic system except an electron capture detector was used to detect the halogenated compounds. Bromonaphthalene was used as an internal standard for these analyses.

Analysis of Saturate, Aromatic and Halogenated Hydrocarbons in Suspended Particulate Matter

Samples of suspended matter from Puget Sound were soxhlet extracted with benzene/methanol according to a published procedure (Clark and Finley, 1973). Concentrated hexane extracts (1 ml) were separated into saturate and aromatic hydrocarbon fractions and analyzed qualitatively and quantitatively by capillary gas chromatography for the presence of saturate, aromatic and halogenated hydrocarbon compounds as previously described for analysis of water. The higher molecular weight PAH (fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene and perylene were positively identified by gas chromatographic comparison with known standards and GC/MS analysis (Fig. B-4).

Preliminary Characterization of Halogenated Hydrocarbons by Capillary Gas Chromatography/Mass Spectrometry

Chemical characterization of halogenated compounds associated with suspended matter from Puget Sound was conducted using a Hewlett Packard 5840-A gas chromatograph containing a 30 meter SP-2100 glass capillary column operating in the splitless mode and coupled to a Hewlett Packard 5985 GC-Mass Spectrometer equipped with 7900A and 7920 disc drives operating in the electron impact mode. Samples contained in heptane were injected into the gas chromatograph at 70°C, held at the temperature for 4 minutes and programmed at 4°/min to a final temperature of 250°C. Tentative assignment of molecular and structural formulas to halogenated compounds was based on comparison of chlorine isotope ratios of the unknown compounds to those reported by McLafferty (1967).

Quantitation of Halogenated Compounds in Suspended Matter and Water from Blair Waterway and Hylebos Waterway by Electron Capture Gas Chromatography

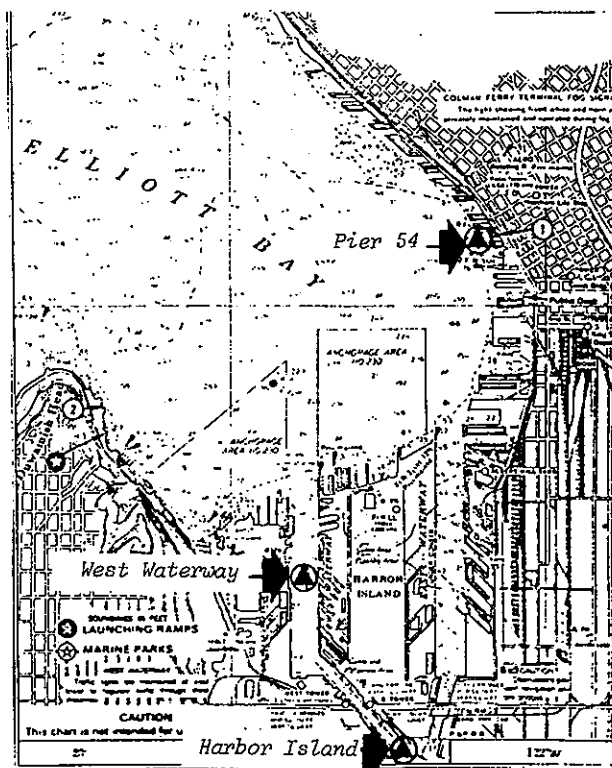
Halogenated hydrocarbons for which analytical standards were available were quantitated using an electron capture detector that had been calibrated within a concentration range indicated to fit the regions of concentrations of the unknowns.

Figure B-4. Total ion chromatogram (TI) and single ion reconstruct of fluoranthene (1, MW202), pyrene (2, MW202), benz(a)anthracene (3, MW228), chrysene (4, MW228), benzo(a)pyrene (5, MW252) and perylene (6, MW252).

APPENDIX C
LOCATIONS OF SAMPLING AREAS AND SAMPLING STATIONS
IN PUGET SOUND

ELLIOT BAY AREA

Stations: Pier 54
Harbor Island
West Waterway



SINCLAIR INLET AREA

Bremerton Station

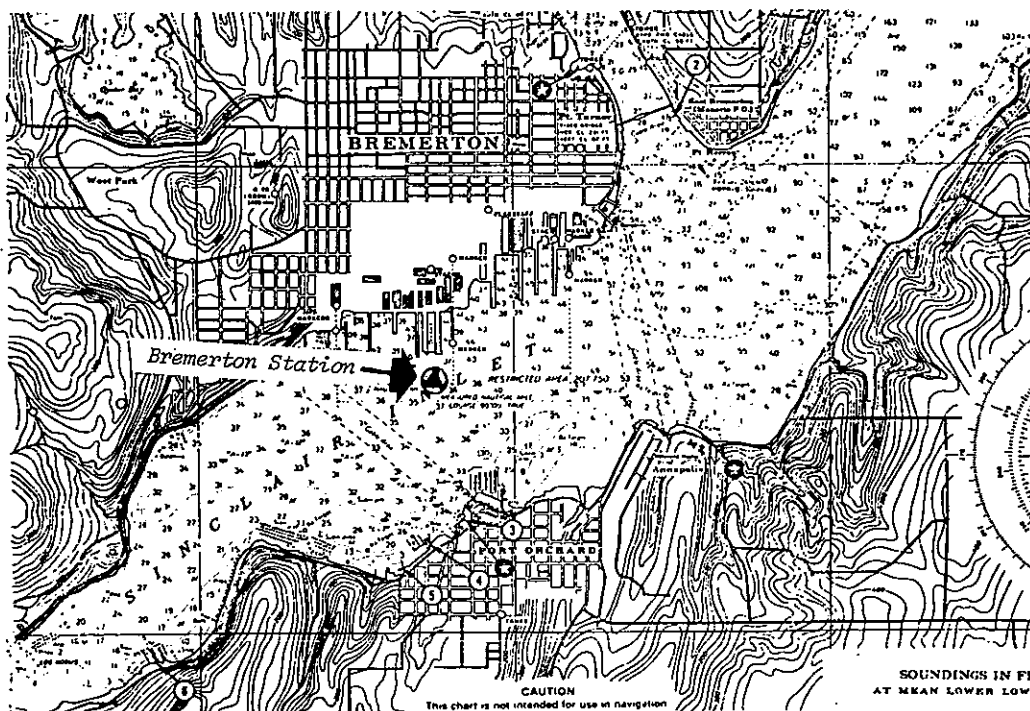
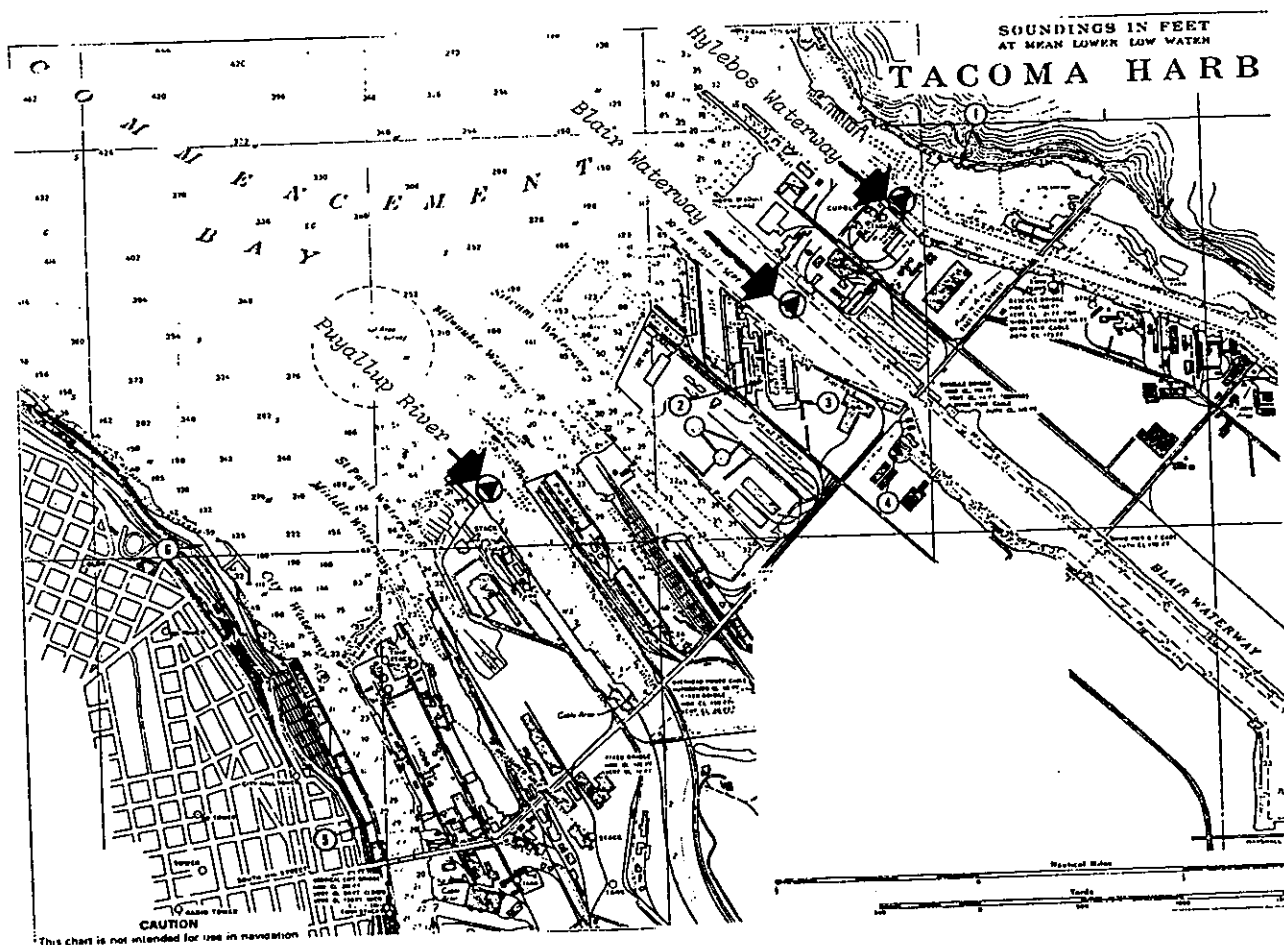


Figure C-1. Maps of Elliott Bay area and Sinclair Inlet area showing locations of Pier 54, Harbor Island, West Waterway and Bremerton sampling stations.



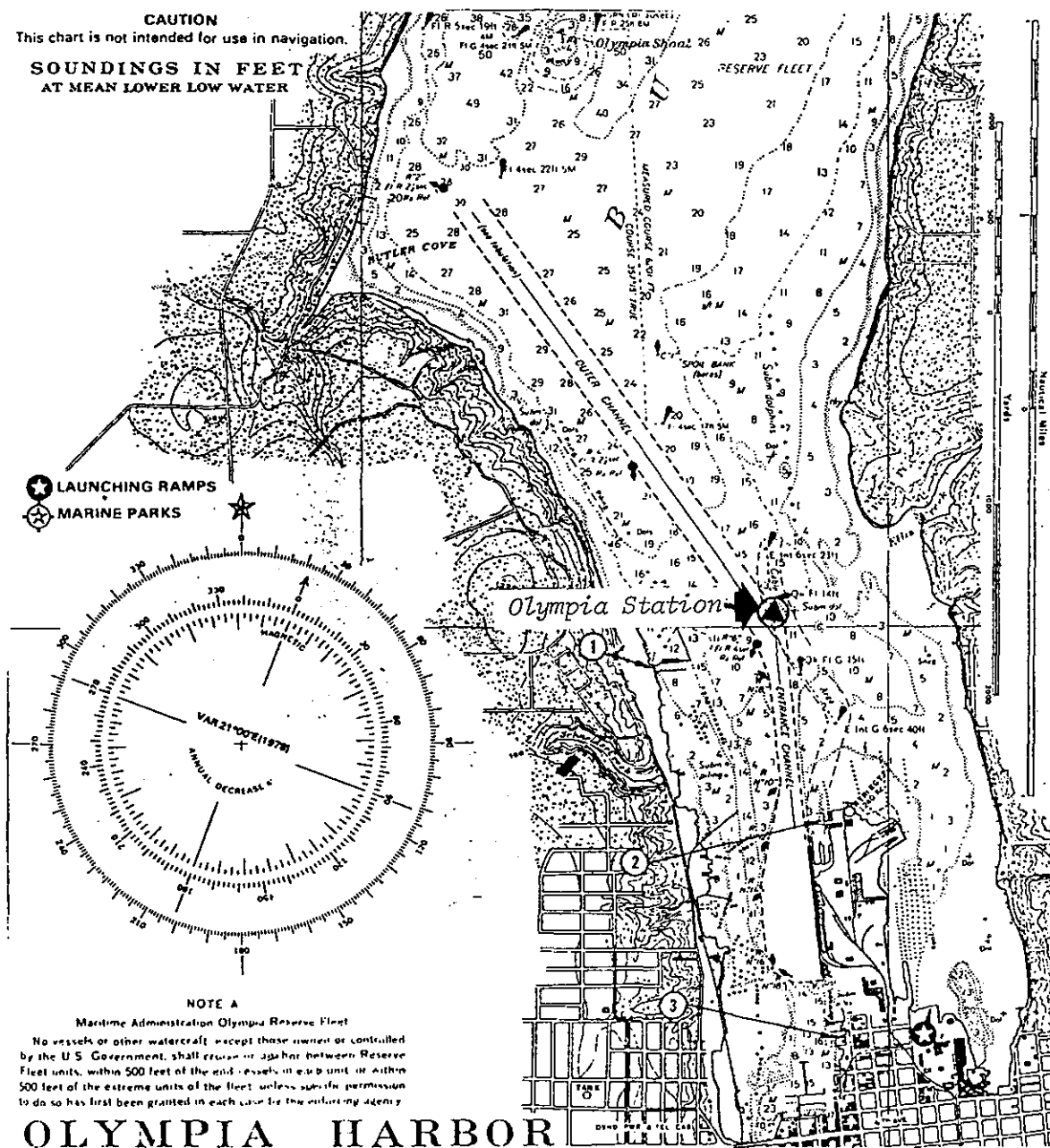
COMMENCEMENT BAY AREA

Stations: Puyallup River
Hylebos Waterway
Blair Waterway

Figure C-2. Map of Commencement Bay area showing locations of Puyallup River, Hylebos Waterway and Blair Waterway sampling areas.

CAUTION
This chart is not intended for use in navigation.

**SOUNDINGS IN FEET
AT MEAN LOWER LOW WATER**



OLYMPIA HARBOR

BUDD INLET AREA

Olympia Station

Figure C-3. Map of Budd Inlet area showing locations of Olympia sampling station.

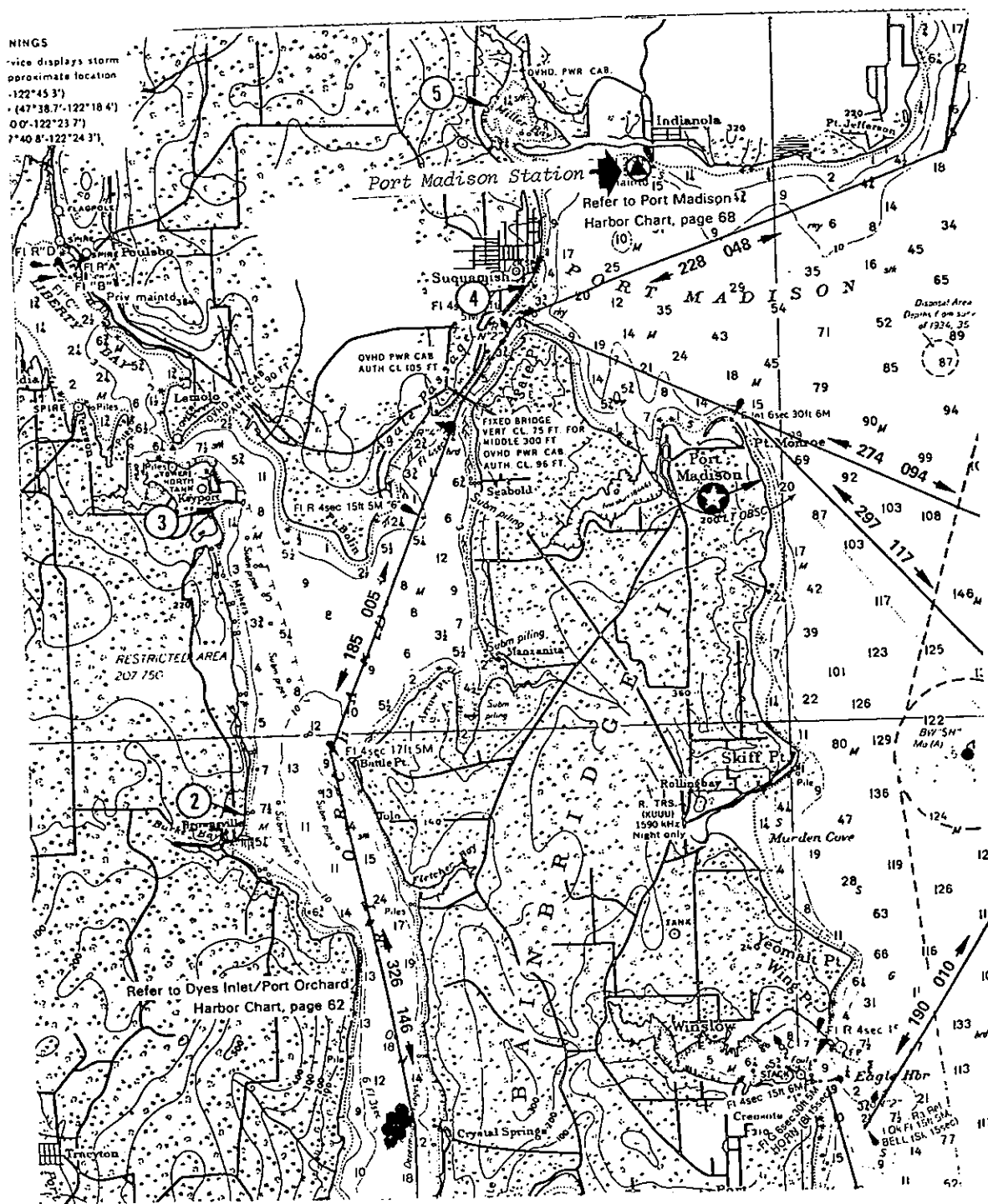


Figure C-4. Map of Port Madison area showing location of Port Madison sampling station.

APPENDIX D

MASS SPECTRA OF HALOGENATED COMPOUNDS ISOLATED FROM
SUSPENDED MATTER FROM HYLEBOS WATERWAY

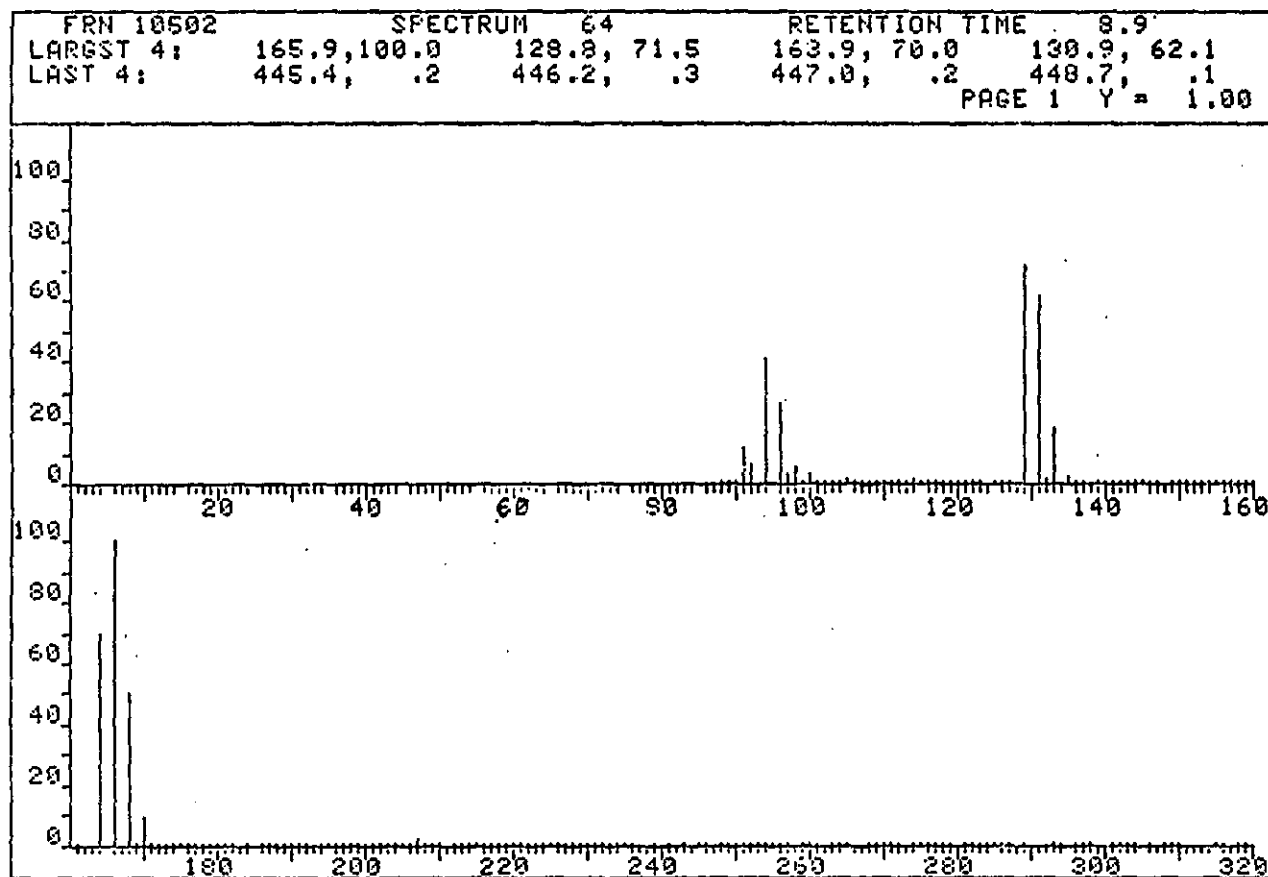


Figure D-1. Mass spectrum of tetrachloroethylene (compound a of Figure 16).

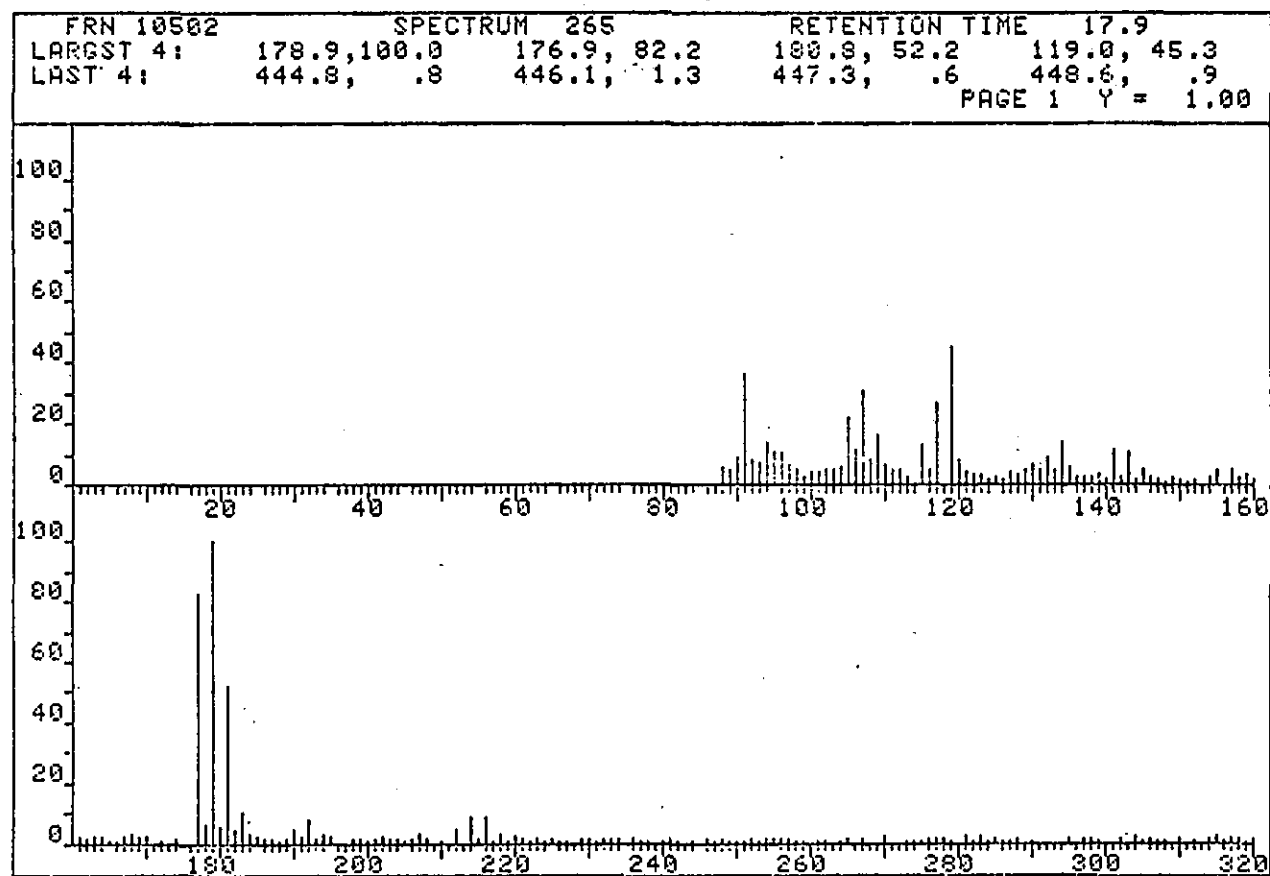


Figure D-2. Mass spectrum of pentachloropropene isomer (compound b of Figure 16).

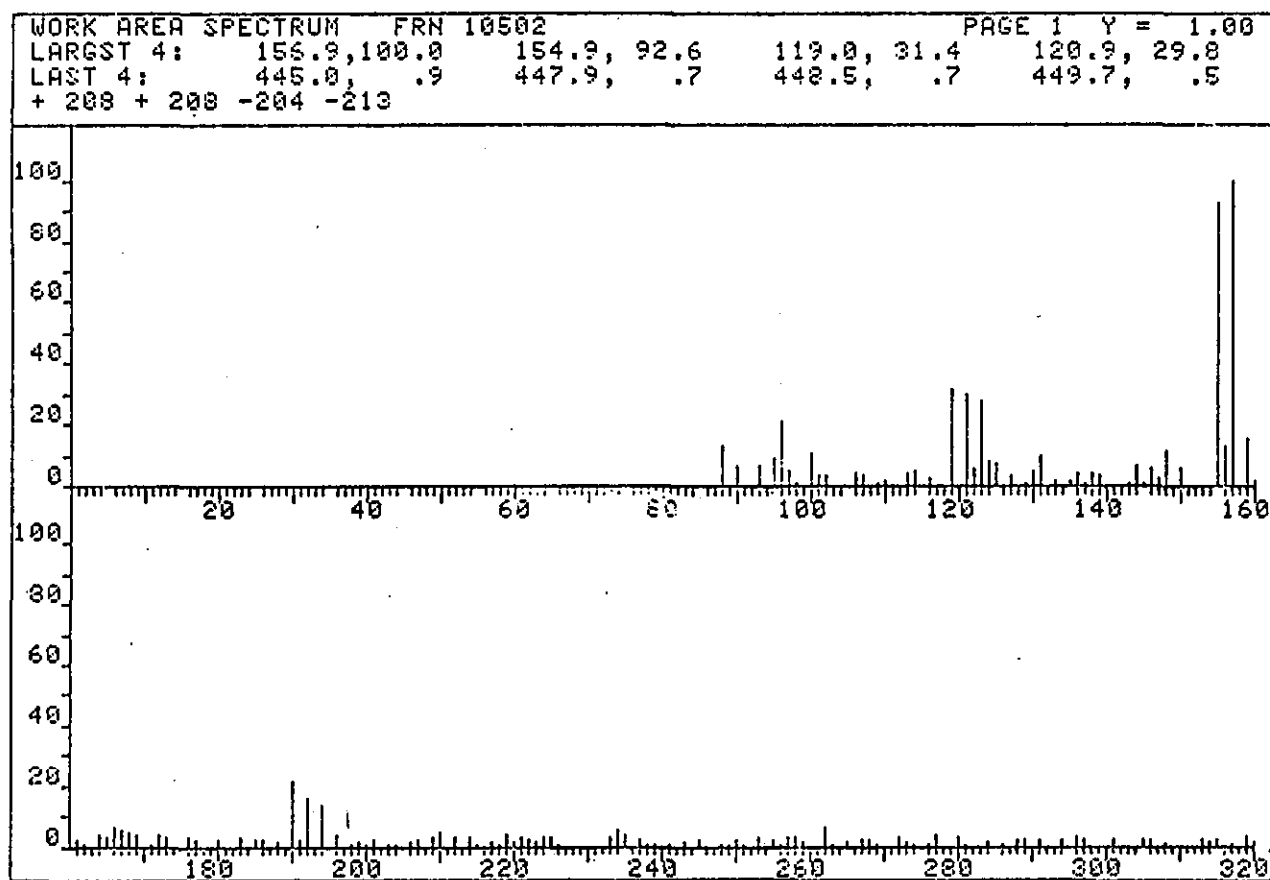


Figure D-3. Mass spectrum of tetrachlorobutadiene isomer (compound c of Figure 16).

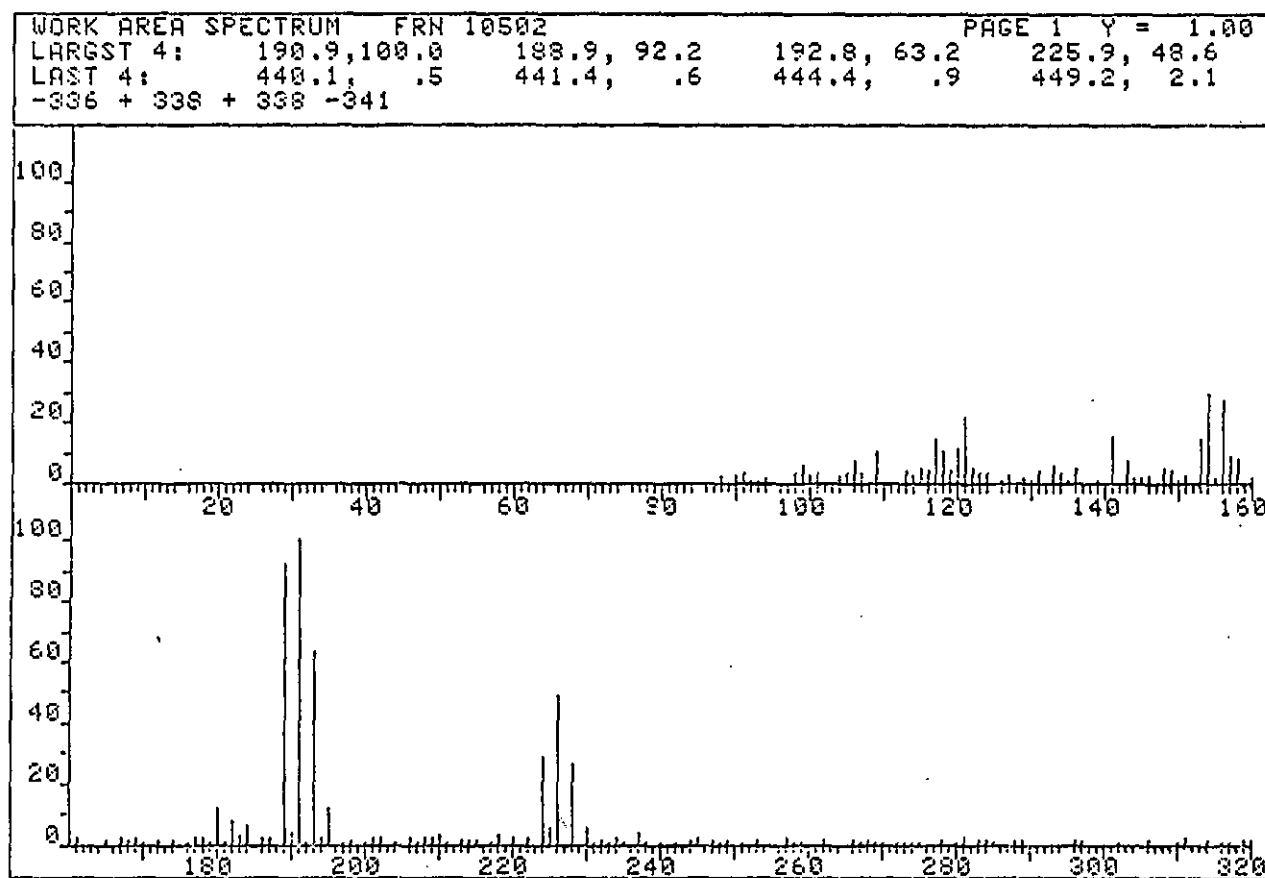


Figure D-4. Mass spectrum of pentachlorobutadiene isomer (compound d of Figure 16).

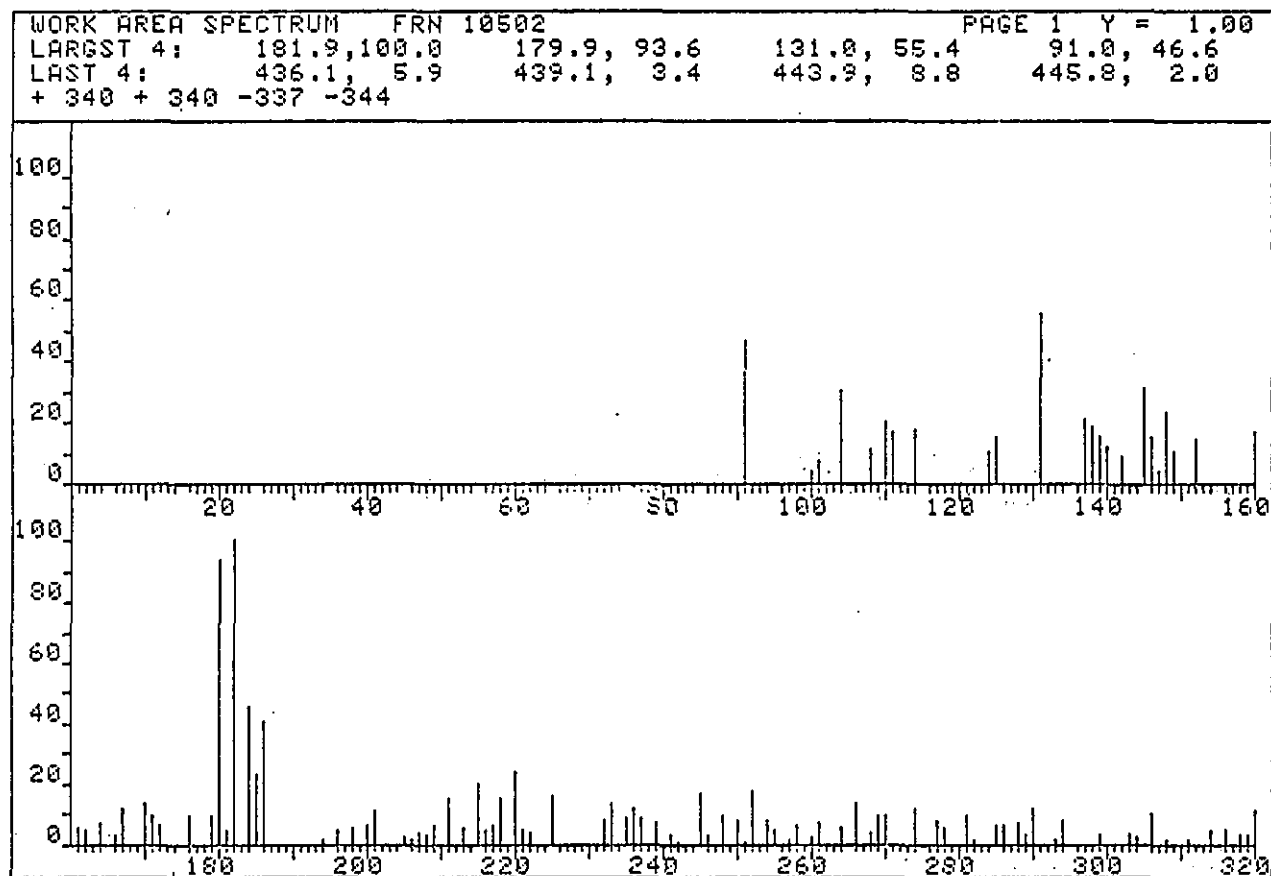


Figure D-5. Mass spectrum of trichlorobenzene isomer (compound e in Figure 16).

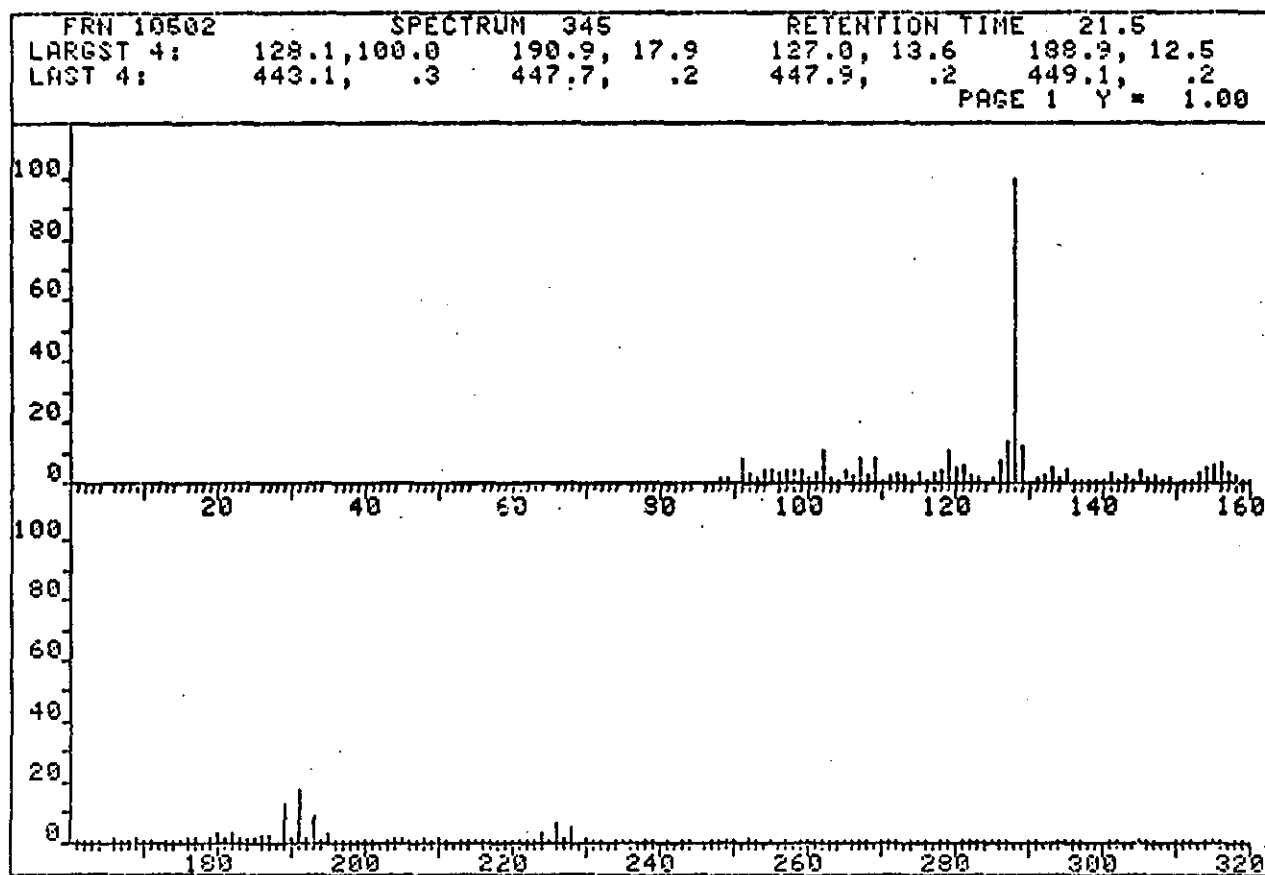


Figure D-6. Mass spectrum of pentachlorobutadiene isomer (compound f in Figure 16).

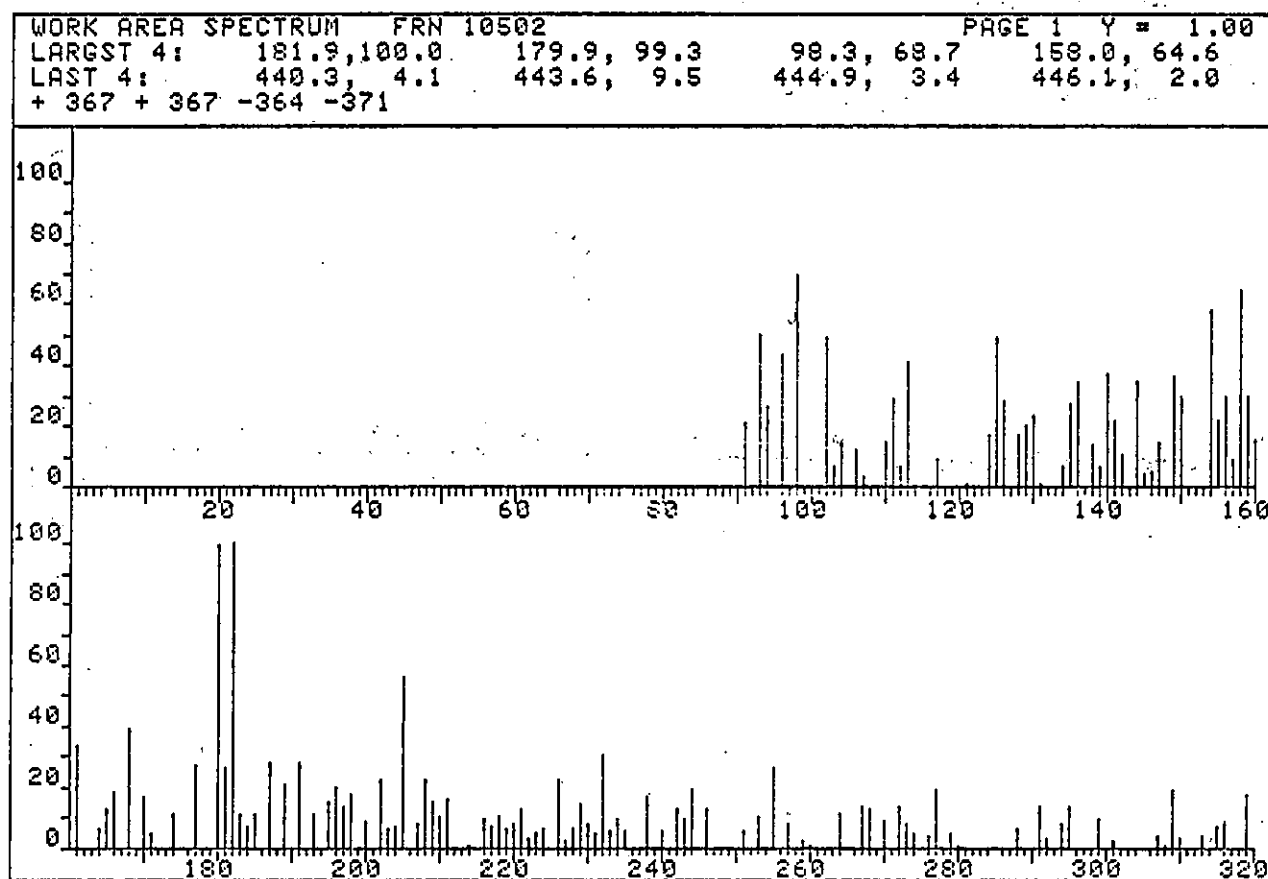


Figure D-7. Mass spectrum of trichlorobenzene isomer (compound g in Figure 16).

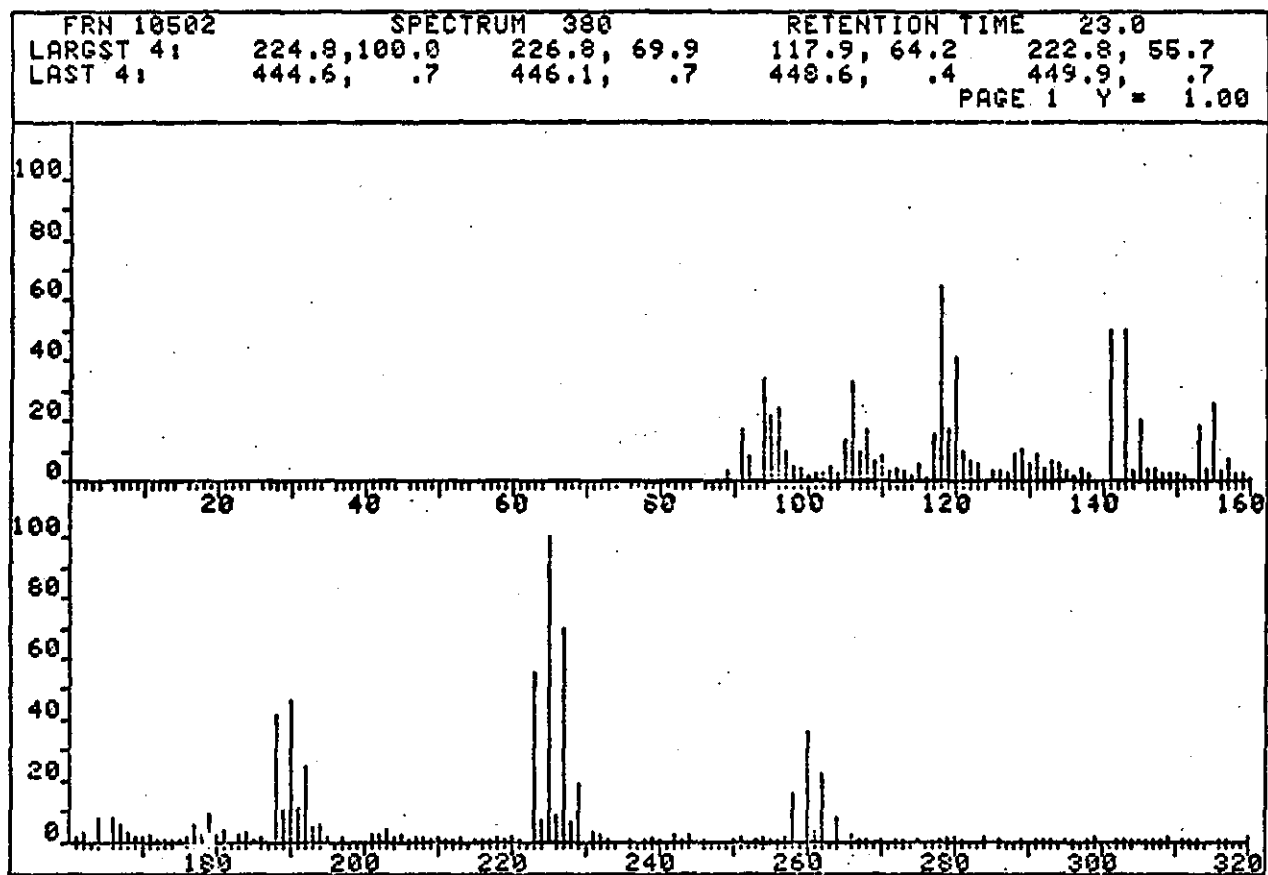


Figure D-8. Mass spectrum of hexachlorobutadiene (compound h in Figure 16).

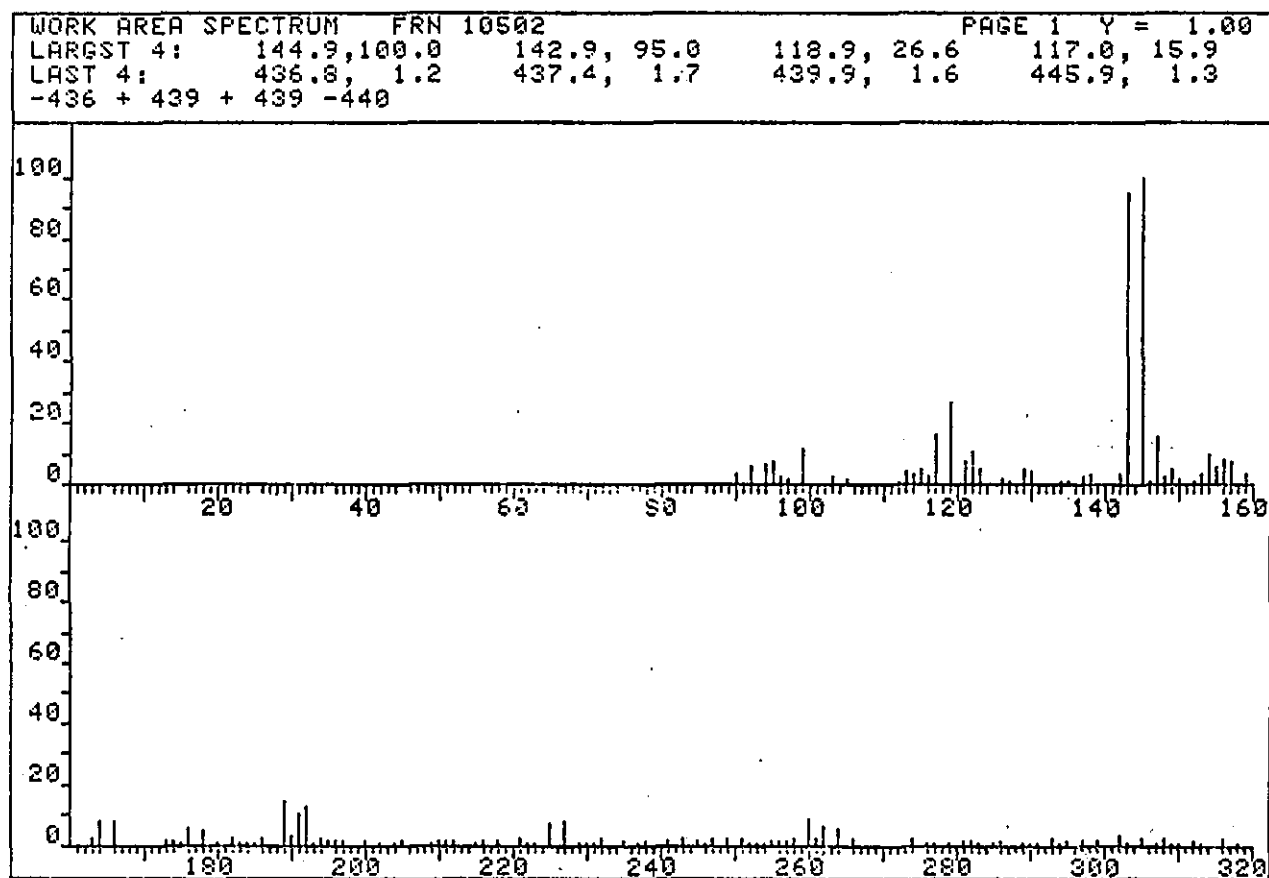


Figure D-9. Mass spectrum of hexachlorobutene isomer (compound i in Figure 16).

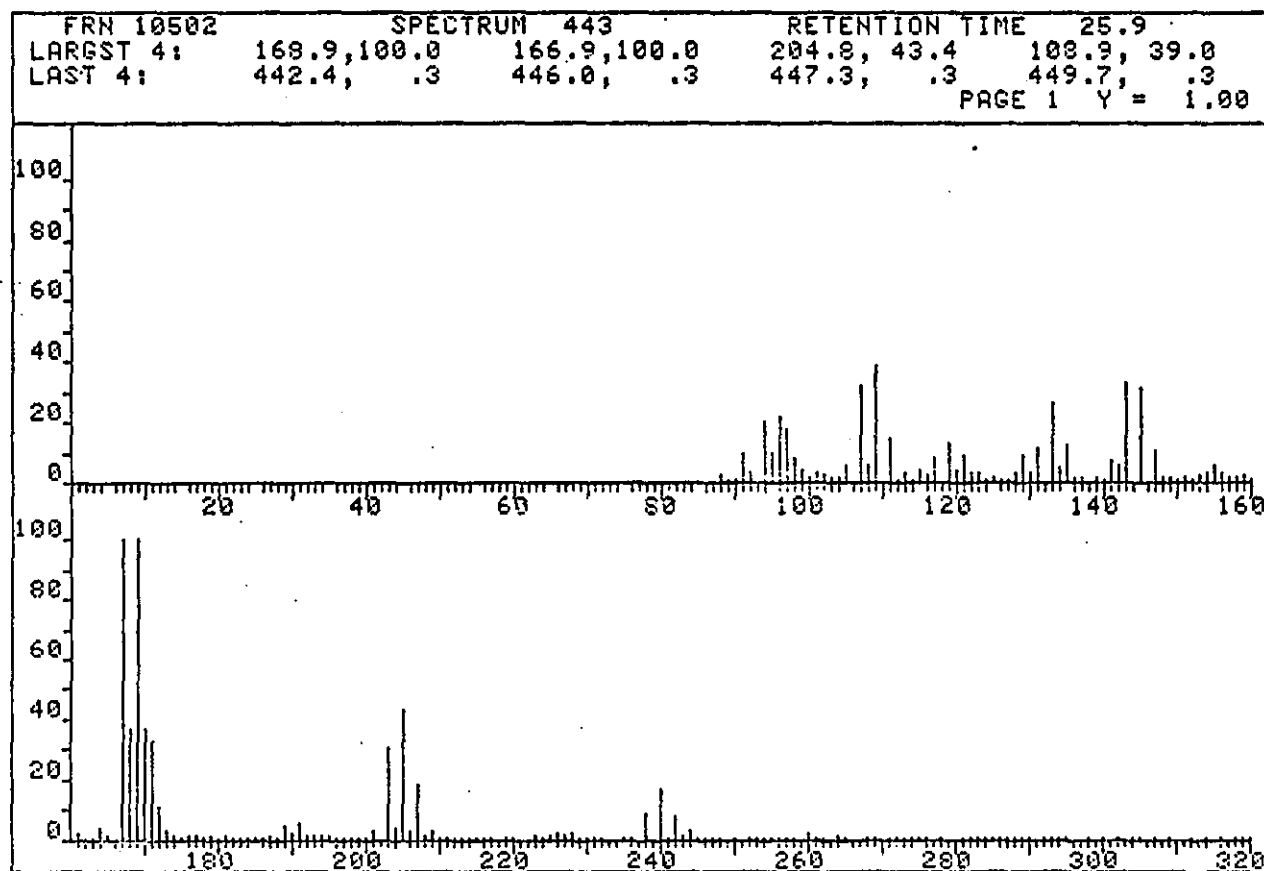


Figure D-10. Mass spectrum of pentachloropentadiene or pentachlorocyclopentene isomer (compound j of Figure 16).

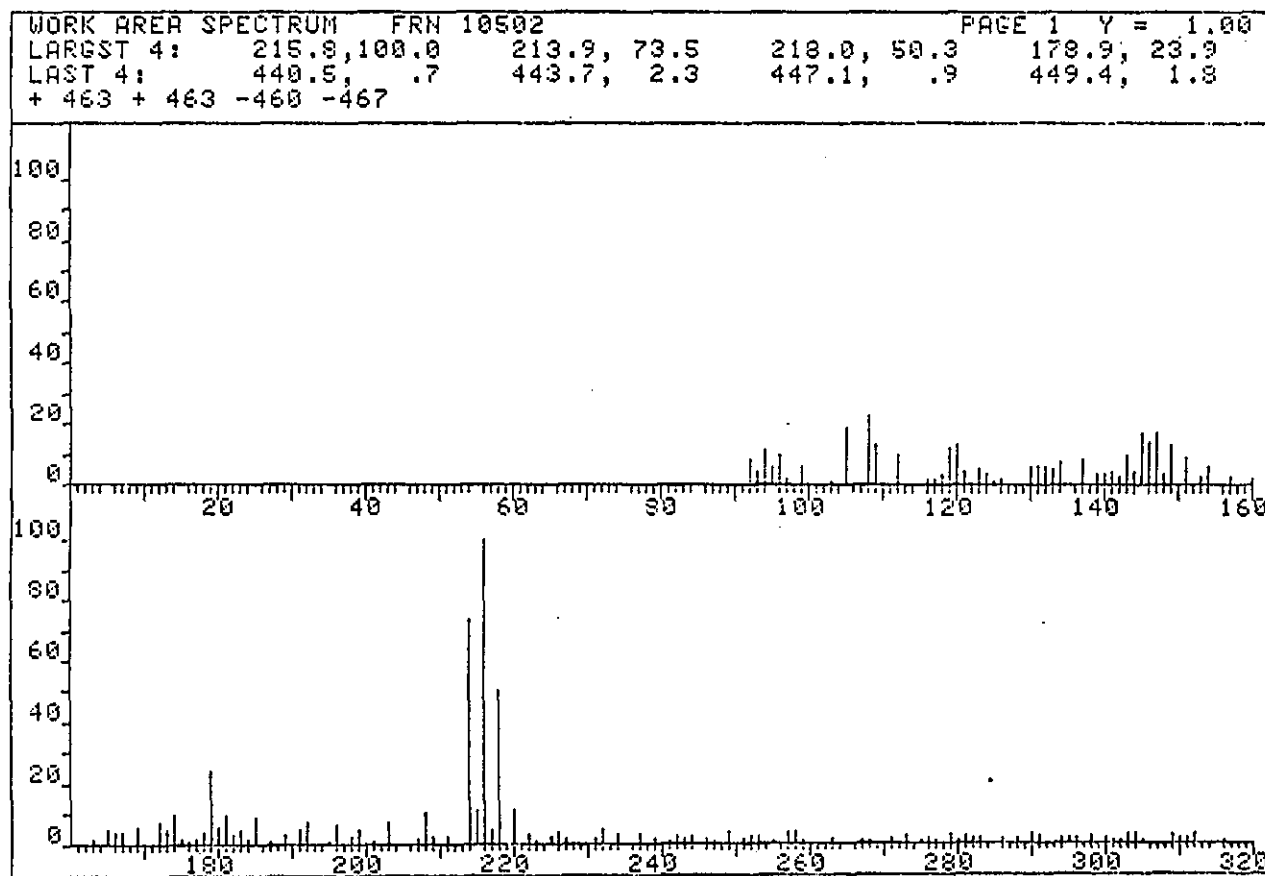


Figure D-11. Mass spectrum of tetrachlorobenzene isomer (compound k in Figure 16).

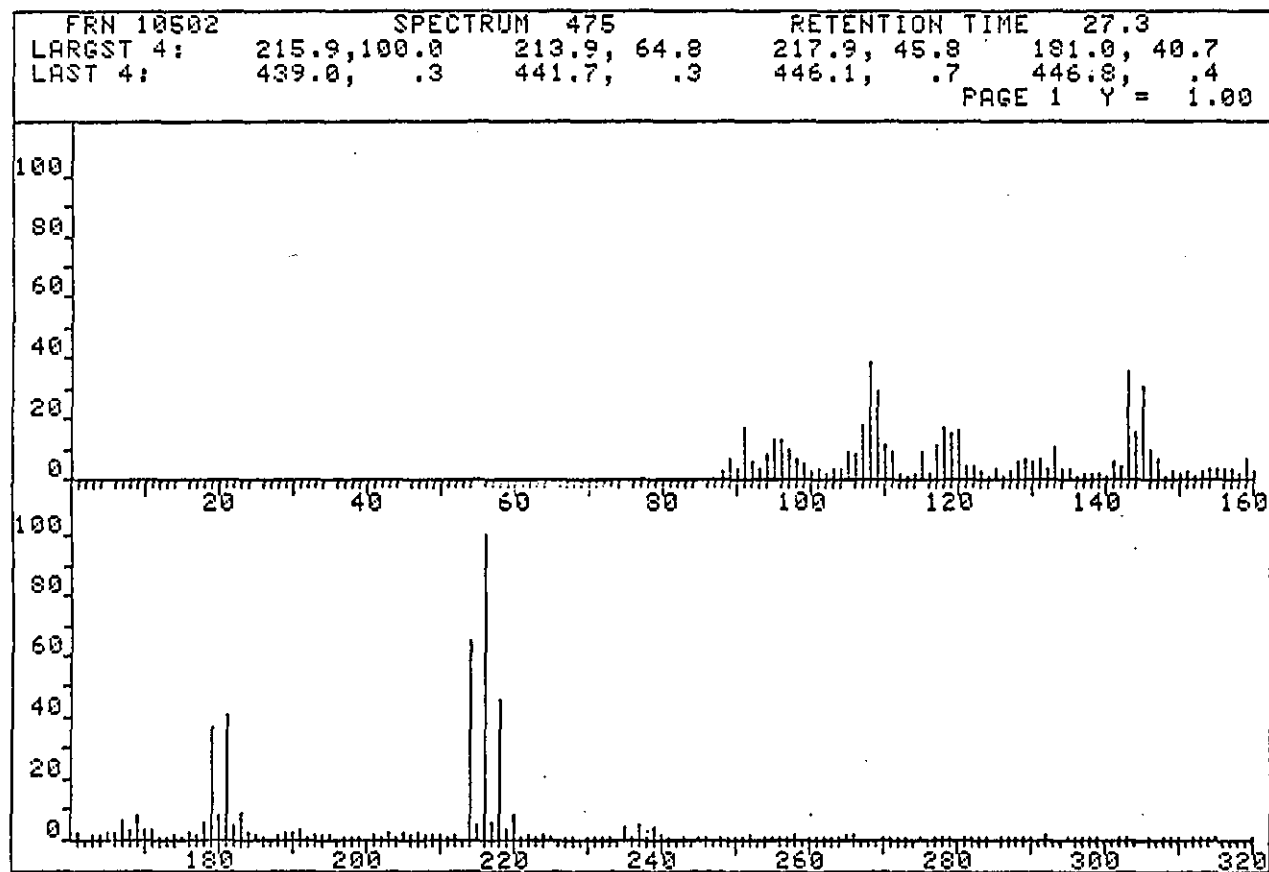


Figure D-12. Mass spectrum of tetrachlorobenzene isomer (compound 1 in Figure 16).

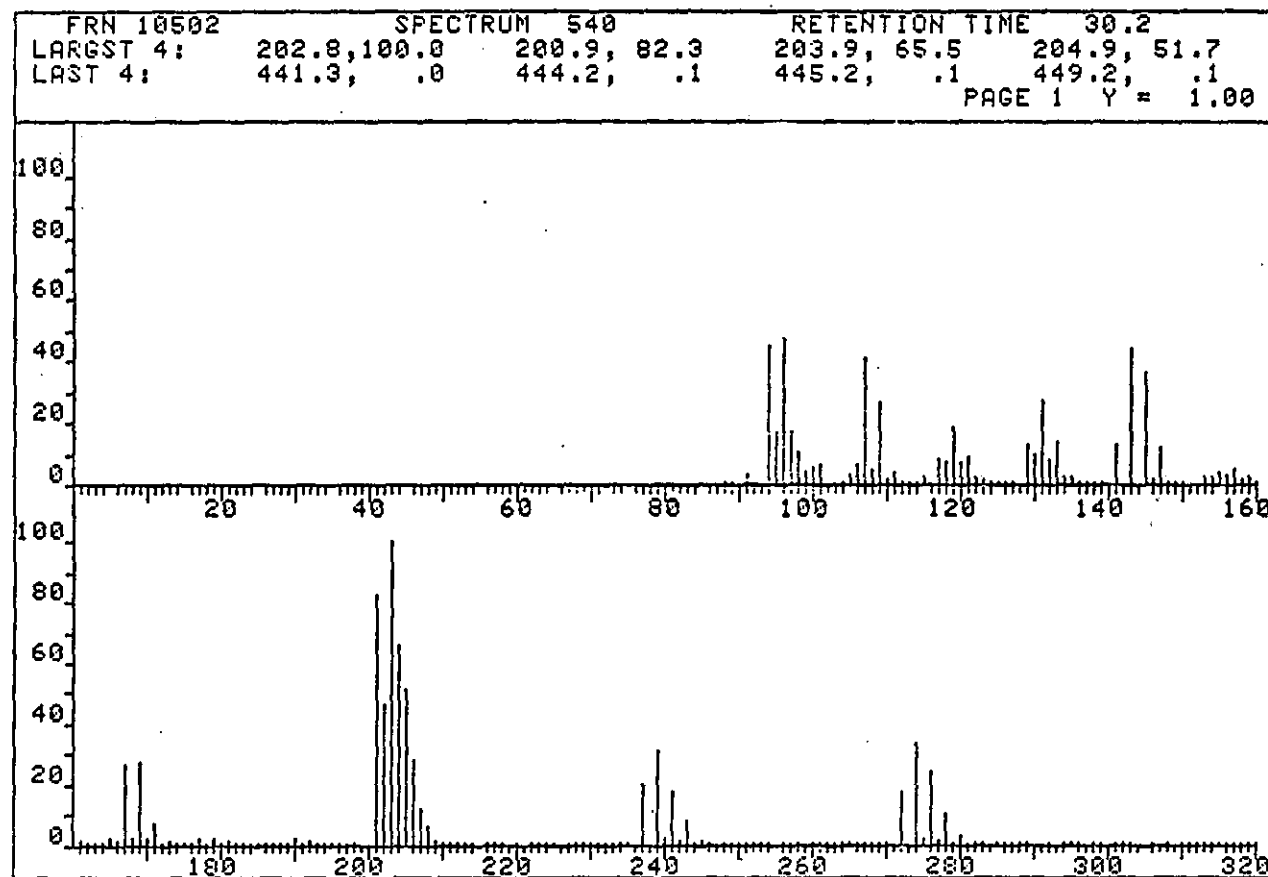


Figure D-13. Mass spectrum of hexachloropentadiene or hexachlorocyclopentene isomer (compound m in Figure 16).

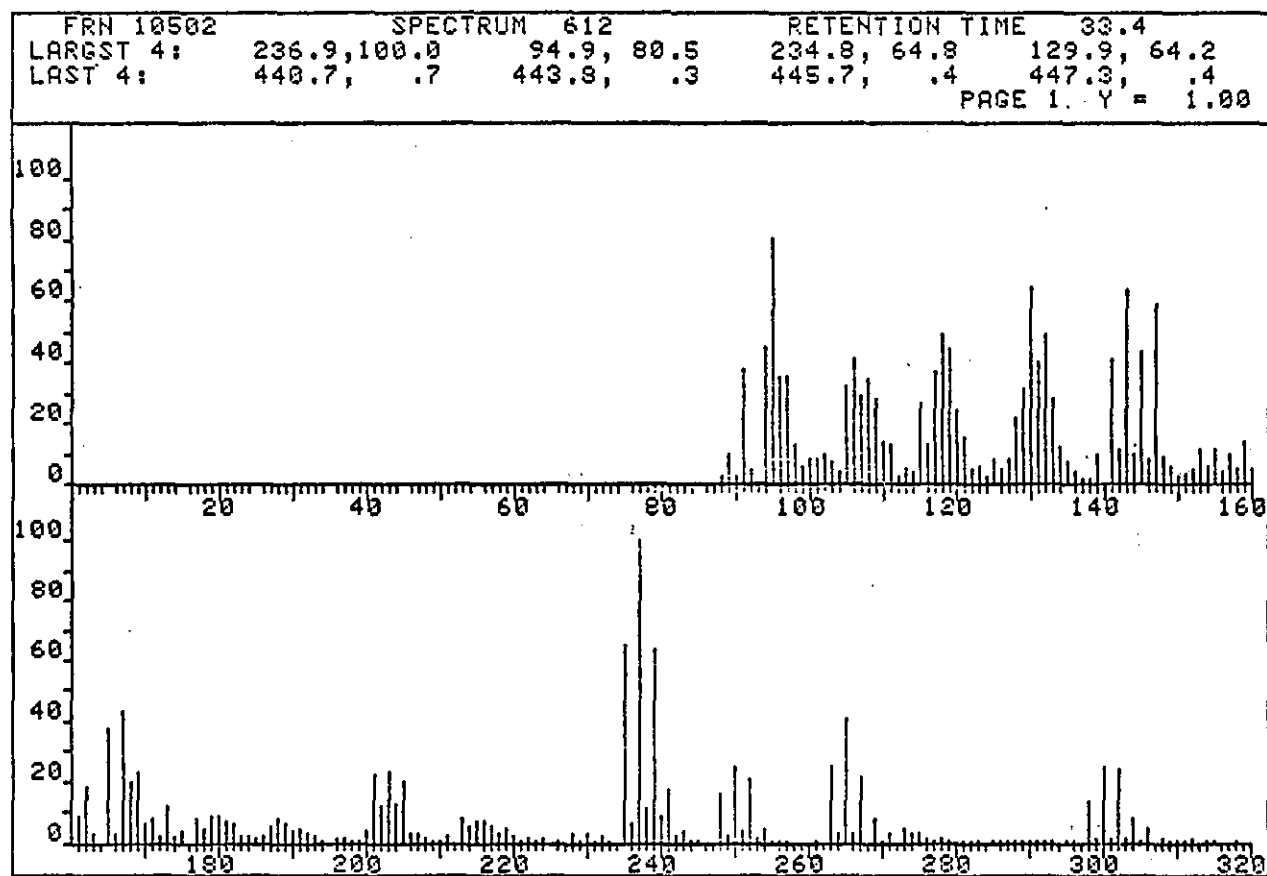


Figure D-14. Mass spectrum of mixture of hexachloroheptatriene and pentachlorobenzene isomers (compound n in Figure 16).

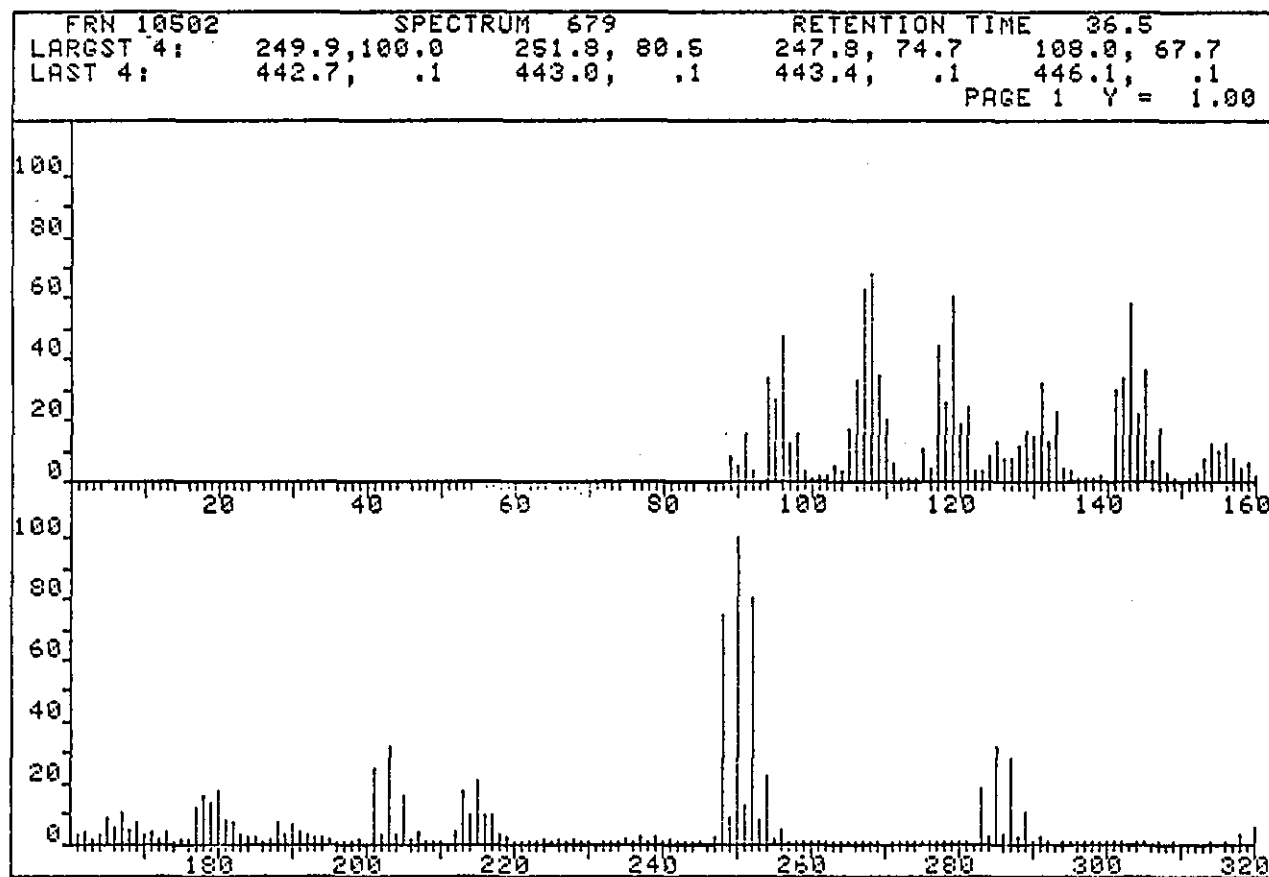


Figure D-15. Mass spectrum of heptachlorohexatriene or heptachlorocyclohexadiene isomer (compound o in Figure 16).

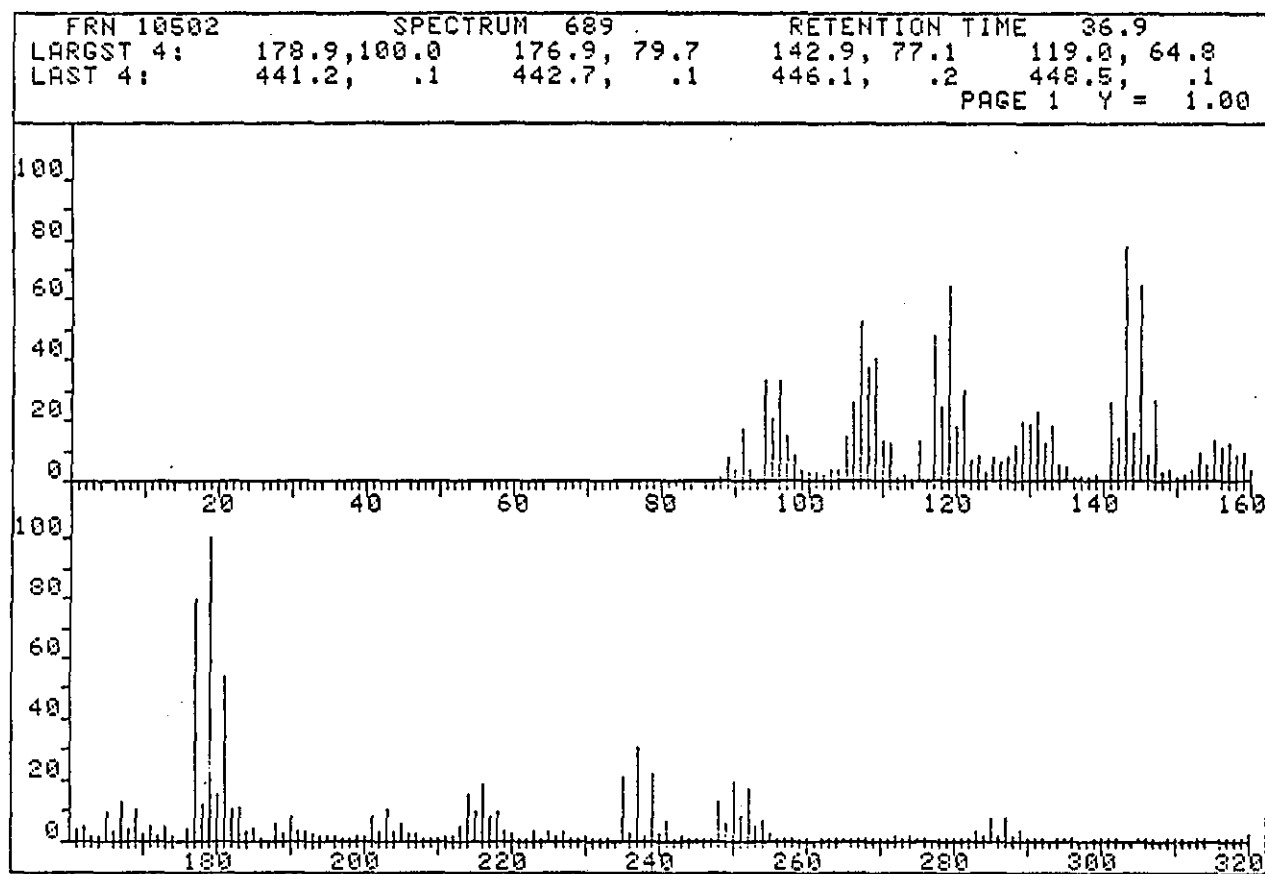


Figure D-16. Mass spectrum of heptachlorohexatriene or heptachlorocyclohexadiene isomer (compound p in Figure 16).

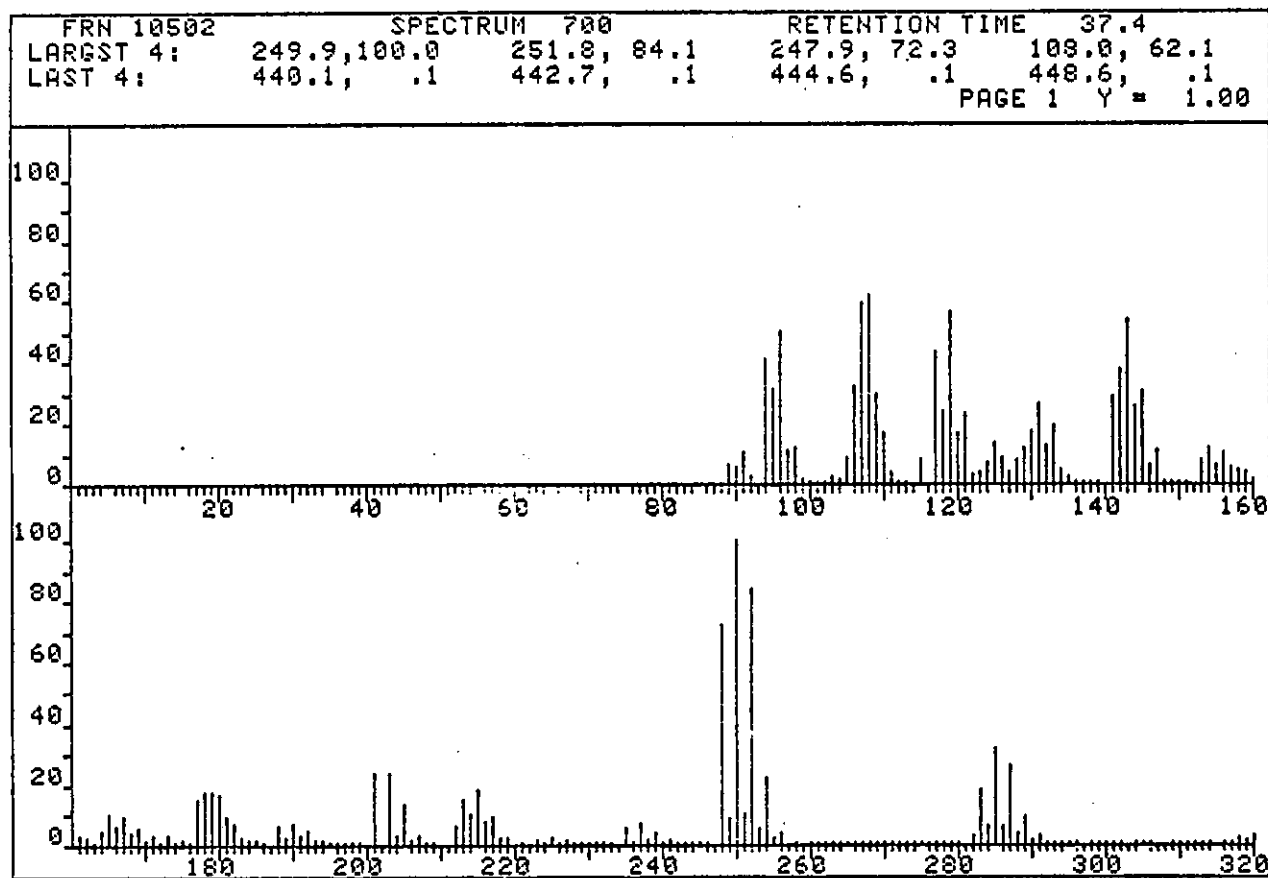


Figure D-17. Mass spectrum of heptachlorohexatriene or heptachlorocyclohexadiene isomer (compound q in Figure 16).

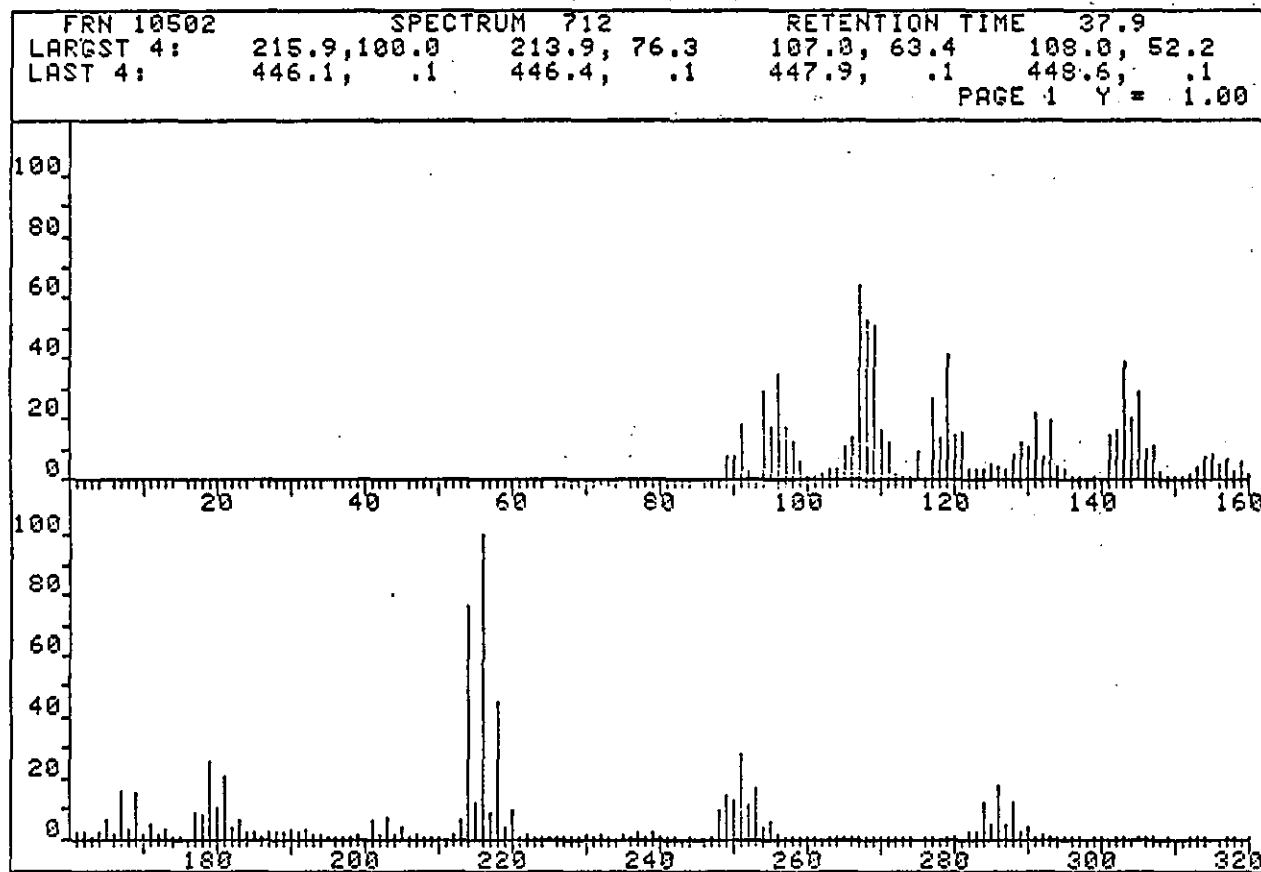


Figure D-18. Mass spectrum of hexachlorocyclohexadiene or hexachlorohexatriene isomer (compound r in Figure 16).